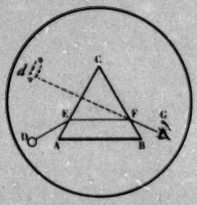

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SOME PROBLEMS IN THE SPECTROSCOPY OF COMPLEX MOLECULES

S. I. Kubarev

Received 18 July 1959

It is shown that the fundamental spectroscopic manifestations of complex molecules can be understood from a single viewpoint. In connection with this, the general problem is stated. Possible explanations are given of the origin of absorption continua in the spectra of complex molecules. It is shown that the applicability of the oscillator approximation to complex molecules permits the explanation of the experimentally observed temperature dependence of band intensities.

According to a proposed classification,[1] a polyatomic molecule belongs to the class of complex molecules if the degree of interaction between the normal vibrations is such that it leads to a continuous region of vibrational energy. The proposed definition of complex molecules results from an analysis of electronic spectra and the necessity of explaining their continuous nature, characteristic of the overwhelming majority of molecules. The positive aspect of such a classification is that it underscores the role of the internal properties of complex molecules in determining the spectra, while the influence of the solvent and of other factors is considered to be of secondary importance. We note that, in reality, the concept of continuous vibrational regions is an approximation. It is due mainly to the complexity of the molecule (large number of degrees of freedom) and, strictly speaking, does not occur. The discreteness of the infrared spectra of complex molecules[2] substantiates the above contention.

With the accumulation of experimental data on the electronic spectra of complex molecules, opinion crystallyzed concerning the existence of two types of spectra: modulation spectra and spectra of attenuation.[3] Sometimes this division is related to the symmetry type, although some work has already appeared in the literature[4] questioning the expediency of such a classification. It is usually considered that modulation spectra correspond to relatively weak interactions between electrons and nuclei; while in the case of spectra of attenuation, this interaction is so strong that it is impossible to separate, even nominally, the electronic and vibrational energies.[3]

Our opinion is that the distinction between the spectra of attenuation and the modulation spectra is a matter of nomenclature rather than fact, since both can be considered from the viewpoint of the adiabatic approximation. It should be stressed that the concept of a strong interaction between electrons and nuclei does not exclude consideration of states of rapid and slow subsystems. The meaning of the adiabatic approximation consists not in the assumption that the interaction between the electrons and nuclei is weak (its magnitude can be arbitrary), but in the assumption of the absence of energy redistribution between the subsystems. The concept of relaxation of electronic levels would thus lead directly to nonadiabatic behavior.

Careful investigation of the absorption and emission spectra of a large number of molecules[3] led to the conclusion that usually a transition from one type of spectrum to the other occurs with an increase in the effect of a substituent group on the aromatic part of the molecule. At present, it is well known that there do not exist two clearly differentiated types of molecules. It has also been found that a similar transition occurs on strong distortion of the symmetry of the skeleton of several dyes. The general shape of the curve of the quantum yield of fluorescence is qualitatively identical for the two types. The existence of a large number of "transition" molecules must indicate that all the fundamental spectroscopic manifestations of complex molecules (these are concerned first of all with the origin of continuous bands, symmetry relations, absorption and emission band shapes, etc.) should be explainable from a single viewpoint.

We will assume that the adiabatic approximation is applicable to at least some of the lower electronic levels of a complex molecule. In this case, it is easy to derive general relations whose analysis, it is to be hoped, will lead to an explanation of the fundamental spectroscopic manifestations of complex molecules. Indeed, following Lax,[5] let us use the following form for the spectral intensity of absorption and emission

$$I(\nu) = \int \exp(-2\pi i \nu t)\, I(t)\, dt,$$

where the Fourier expressions for absorption and emission are, correspondingly,

$$\left.\begin{aligned} I_{abs.}(t) &= \mathrm{Av}\left\{ M^*_e e^{\frac{it}{\hbar}\hat{H}_b} M_e e^{-\frac{it}{\hbar}\hat{H}_a} \right\}, \\ I_{em.}(t) &= \mathrm{Av}\left\{ M_e e^{-\frac{it}{\hbar}\hat{H}_a} M^*_e e^{\frac{it}{\hbar}\hat{H}_b} \right\}. \end{aligned}\right\} \qquad (1)$$

The symbol Av here indicates the average; M is the transition operator: $\hat{H}_a$ and $\hat{H}_b$ are the vibrational Hamiltonians for the ground and excited electronic levels, respectively.

It is known that in the adiabatic approximation the electronic level is a certain hypersurface. For a slow subsystem in the oscillator approximation, it is possible to introduce the concept of ν_0—the frequency of the purely electronic transition, identical for absorption as well as for emission. In the general case, the concept of ν_0 is indeterminate, since for emission and absorption there exist separate frequency values for the purely electronic transition. Formally, we thus have the scheme of multiple levels proposed by Neporent.[6] Since this is the scheme meant when one mentions attenuation spectra, then it can be seen that one should talk rather about the failure of the oscillator approximation than the impossibility of separate consideration of electronic and vibrational energies. In connection with this, the investigation of the polarization properties of spectra of complex molecules is very important. The fact that, according to the existing experimental data,[3] the polarization spectra of the two spectral classes do not differ appreciably from each other is a point possibly in favor of the oscillator approximation. Discovery of molecules with different properties would be of great interest, mainly for the scheme of multiple levels, which in principle can be the key to the understanding of polarization spectra. There exists a certain difficulty in the case of attenua-

tion spectra,[4] consisting of the fact that the molecules to which these spectra are ascribed, exhibit, as a rule, large luminescence quantum yields. This seems to be a straightforward indication that the deviation from adiabatic behavior is small and that the concept of relaxation of electronic levels must be replaced by the usual vibrational relaxation. In the adiabatic approximation, this difficulty is, of course, absent.

Let us now examine some general conclusions following from (1). One of the possible explanations for the origin of continuous bands can be that during absorption or emission of light in a rapid subsystem a part of the vibrational degrees of freedom can be considered semiclassically. Physically this means that the terminal states correspond to large quantum numbers and hence, according to the correspondence principle, can be considered classically. Such an analysis can be applied to relatively small frequencies and also to the case of large shifts in equilibrium positions in the ground and excited states. In other words, the semiclassical approximation can be realized only if the interaction between the electrons and the nuclei is sufficiently strong. Let us note that in a number of cases the semiclassical approximation can be used formally, since interaction between the various bonds broadens the levels in the excited state.

Another explanation is possible, more applicable to molecules where it is not possible to assume the presence of strong interaction between the electrons and the nuclei. The optically active electrons in a complex molecule (for example, π-electrons) always interact with only a part of the molecule's skeleton. Division of the molecule into separate parts, one related to absorption and the other one serving as a heat reservoir, has been done before in the literature.[7]

It is important to note that, at the same time, there is no need to postulate strong anharmonicity in order to describe strong interaction between the two parts. Indeed, if one denotes the sum total of the normal coordinates of the optically active part through x and the sum total of the normal coordinates of the reservoir through y, then the vibrational Hamiltonians can be written down in the following form

$$\left.\begin{aligned}\hat{H}_a &= \hat{H}_a(x) + \hat{H}(y) + \sum A_{jk} x_j y_k + \dots,\\ \hat{H}_b &= \hat{H}_b(x) + \hat{H}(y) + \sum B_{jk} x_j y_k + \dots\end{aligned}\right\} \qquad (2)$$

It can be seen from the above that strong interaction between the two parts is guaranteed already in the linear approximation by the y coordinates.

If the number of normal vibrations corresponding to the y coordinates is small, then the semiclassical approximation is at least formally applicable, thus leading to washing-out of structure. In this case

$$\begin{aligned} I(t) = \mathrm{Av}\Big\{&\Big(\exp\frac{it}{\hbar}\sum B_{jk}x_j y_k\Big)\cdot M^{*}\Big(\exp\frac{it}{\hbar}\hat{H}_b(x)\Big)\\ &\times M\Big(\exp-\frac{it}{\hbar}\hat{H}_a(x)\Big)\cdot\Big(\exp-\frac{it}{\hbar}\sum A_{jk}x_j y_k\Big)\Big\}. \end{aligned} \qquad (3)$$

Each line in the electronic-vibrational transition corresponding to the electronic transition a → b will be broadened. It can be seen from (3) that the broadening is determined by averaging over y.

At the same time, an expression in the form of (2) is really the basis of the oscillator approximation for complex molecules. But then definite conclusions about the temperature dependence of the band intensities of complex molecules can be made since, in this case, (1) can be evaluated accurately.

If, during the electronic transition, the frequencies of the oscillators remain constant and M = const., then,[5,6]

$$\begin{aligned} I^{0}_{\mathrm{abs.}}(t) = \exp\Big\{&2\pi i\nu_{ba}^{0}t + \sum_j |w_j|^2\Big[\big(e^{-i\omega_j t}-1\big)\\ &+\frac{e^{i\omega_j t}+e^{-i\omega_j t}-2}{e^{\beta\hbar\omega_j}-1}\Big]\Big\}. \end{aligned} \qquad (4)$$

Here w_j is a variable proportional to the shift in equilibrium distances. If both the frequencies and the equilibrium distances change, then for M = const. (assuming that the change in frequencies is small) we shall have[8]

$$\begin{aligned} I_{\mathrm{abs.}}(t) &= I^{0}(t)\cdot\exp\Big\{\sum_j -\frac{it}{2}\Gamma_j\coth\frac{\beta\hbar\omega_j}{2}\Big\},\\ \Gamma_j &= \omega_j(a)-\omega_j(b). \end{aligned} \qquad (5)$$

It is easily seen that in the first case the position of the band maximum does not depend on temperature, while in the second case there exists a weak temperature dependence. Experimentally, the temperature independence of the bands of complex molecules has been known for a long time.[9]

The problem of absorption and emission band shape is solved in principle through calculation using (1). In the oscillator approximation, the calculations can be fully performed. If one turns to approximate methods of calculation, such as the semiclassical, then the number of problems which can be solved increases sharply. In the general case, however, it is evident that the semiclassical approximation cannot be applied to all the oscillators in a complex molecule. In this approximation, one can only expect to obtain the approximate contour of the spectrum. This can be seen directly if (1) is transcribed in the following form (M = const.):

$$\begin{aligned} I_{\mathrm{abs.}}(t) &= \mathrm{Av}\exp_{[-]}\Big\{\frac{i}{\hbar}\int_0^t U\Delta E U^{-1}(s)\,ds\Big\},\\ \Delta E &= \hat{H}_b-\hat{H}_a;\quad U(s)=\exp\frac{is}{\hbar}\hat{H}_a. \end{aligned} \qquad (6)$$

The semiclassical approximation corresponds to taking into consideration only the first member of the expansion

$$U\Delta E U^{-1} = \Delta E + \frac{is}{\hbar}[\hat{H}_a\Delta E] + \frac{1}{2!}\Big(\frac{is}{\hbar}\Big)^2[\hat{H}_a[\hat{H}_a\Delta E]]+\dots \qquad (7)$$

Inclusion of several subsequent terms improves the approximate contour and, in particular, automatically takes into consideration the deviations from the Franck-Condon principle.

If the formal application of the semiclassical approximation to the solution of the problem of broadening seems natural enough, such an approach is far from evident when considering the problem of band shape. The semiclassical approximation can strongly distort the true band shape. The fact that the band shape must be determined quantum-mechanically, follows also from reference 5. Thus, in the linear representation of the difference $\hat{H}_b - \hat{H}_a$ an asymmetric band is obtained only through a quantum-mechanical calculation, while the semiclassical approximation leads to a Gaussian shape. In connection with this, let us note that the methods of calculation of band shapes proposed earlier[5,10] are, in fact, identical to the semiclassical approximation, and hence do not have a strict theoretical basis.

In conclusion, the author would like to thank N. D. Sokolov for his interest in the present work.

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EFFECT OF FOREIGN GASES ON THE INTENSITY OF THE ELECTRONIC ABSORPTION OF 3-DIMETHYLAMINO-6-AMINOPHTHALIMIDE VAPOR

S. O. Mirumyants and B. S. Neporent

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A study was made of the effect of a large group of different foreign gases (monatomic He, Ne, A, Kr, Xe, diatomic H_2, D_2, N_2, O_2, CO, NO, triatomic H_2O, D_2O, and polyatomic NH_3, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_5H_{12}) on the intensity of the electronic absorption spectrum of 3-dimethylamino-6-aminophthalimide vapor. It was established that the general behavior of the phenomenon agrees with the results of earlier studies of the authors and is described by the kinetic mechanisms proposed by them. Relative values were determined for the constants which represent the effectiveness of those collisions with foreign particles which are accompanied by a transition of the molecules under study from the normal state to a perturbed state possessing low absorption, or by the reverse transition. It is shown that for the various foreign gases the efficiency of the first process decreases monotonically with an increase in the Van der Waals constant characterizing the molecules of these gases, while the second process is practically independent of the kind of foreign gas molecule. For the case of helium a study was made of the dependence of the effect on the molecular concentration of the substance under study.

The peculiar effect of foreign gases (chiefly light ones) in giving rise to a decrease in the absorption coefficient of β-naphthylamine vapor was observed by one of the authors of the present communication in 1945,[1] and has been the object of further investigations[2-5] in which the principal characteristics of the phenomenon were studied. It was shown that the effect is peculiar to aromatic compounds and hypotheses were formulated concerning the nature of processes which would lead to a weakening of the absorption of the vapor. According to these hypotheses collisions give rise to such large changes of the normal state N of the molecule of the aromatic compound that the conjugation of the π-electron is to a certain extent destroyed (transition to the perturbed state N′). This transition takes place chiefly in "impact" collisions with light molecules; in collisions with heavy molecules, which take place over a finite time interval, this transition is less probable. In reference 4 a kinetic discussion of the process was given; this was based on the hypotheses formulated in references 1 and 3.

In order to obtain new data necessary for the further elucidation of the mechanism of the effect, in the present investigation a study has been made of a large group of foreign gases on the intensity of the electronic spectrum of 3-dimethylamino-6-aminophthalimide vapor, various optical properties of which have already been studied in our laboratory. The rare gases from helium to xenon and also a series of diatomic and polyatomic gases were selected as foreign gases. Preliminary results of the investigation for the rare gases and for certain diatomic gases have been published in reference 5.

Having in mind the attainment of high accuracy and simplicity in the measurements we used the fluorescence method in which, as in reference 1, the integrated intensity of the luminescence of the vapor under study was measured as a function of the amount of foreign gas added. It was verified from special experiments that the shape of the fluorescence spectrum and the fluorescence yield of 3-dimethylamino-6-aminophthalimide vapor for excitation with light of wave length $\lambda_e = 492$ mμ is practically unchanged on adding foreign gases in the pressure interval studied. Small changes of the yield[6] are produced only at foreign gas pressures greatly exceeding those used in the present investigation. The agreement of the results obtained from measurements of the absorption and of the fluorescence was confirmed by direct experiment (cf. Fig. 1). The method of measuring the absorption and fluorescence spectra was described in references 7 and 8. In measuring the integrated intensity of the fluorescence a special photoelectric arrangement was set up. The vapor of the substance under study was contained in a cell similar to that used in the previous investigations.[1] Excitation of the fluorescence was produced by means of an SVDSH-250 mercury lamp, the lines of which were separated with a monochromator. The luminescence was measured with an FEU-18 photomultiplier followed by an amplifier for the photocurrent. The intensity of the exciting light was controlled by means of a special photoelement. The high sensitivity of the arrangement permitted studies to be carried out down to very low vapor pressures of the substance. Measurements of this kind using the absorption method[3] require the use of complicated apparatus.

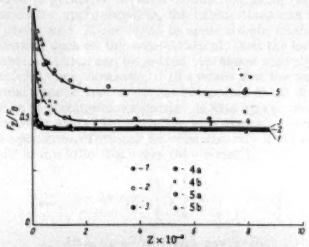

Fig. 1. Effect of helium on the fluorescence intensity F (absorption coefficient ε) of 3-dimethylamino-6-aminophthalimide vapor for different values of the vapor pressure P_N of the latter (T = 528°K). Values of P_N (mm Hg): curve 1—0.00091, curve 2—0.00234, curve 3—0.0054 (a—fluorescence, b—absorption), curve 4—0.0245 (a—fluorescence, b—absorption), curve 5—0.0930 (a—fluorescence, b—absorption).

The following gases and vapors were used as foreign gases: He, Ne, A, Kr, Xe, H_2, D_2, N_2, O_2, CO, NO; H_2O,

D_2O, NH_3; C_2H_4, C_3H_6, C_3H_8, C_4H_{10}, C_5H_{12}. All the experiments were carried out at a temperature of 528°K and at a pressure of 5.4×10^{-3} mm Hg for the 3-dimethylamino-6-aminophthalimide vapor. The experiments on the effect of helium were exceptions; in these the dependence of the effect on the pressure of the 3-dimethylamino-6-aminophthalimide vapor was studied. For the hydrocarbon gases*—oxygen, nitric oxide, and ammonia—only values

*The authors are grateful to Ya. E. Shmulyakovskii and M. I. Dement'evaya for their kindness in furnishing the hydrocarbon gases.

of the weakening of the intensities of the spectrum in the limit of high foreign gas pressures were determined.

The results obtained for the effect of helium are given in Fig. 1, which shows the dependence of the relative intensity of the fluorescence (absorption coefficient) on the number of collisions, Z, of a molecule of the substance under study with helium atoms.* As in the previous

*The value of Z was determined from the well-known formulas of the kinetic theory of gases. The atomic and molecular radii used are given in reference 6.

investigations when the vapor pressure P_N of 3-dimethylamino-6-aminophthalimide is decreased an increase in the effect of helium is observed, that is, the slope of the initial part of the curves increases and the limiting value of the absorption coefficient, expressed in our case as F_∞/F_0, decreases.

For the quantitative interpretation of the results obtained it is expedient to use the expressions derived in reference 4:

$$\frac{\varepsilon_0}{\varepsilon_0 - \varepsilon_e} = \frac{1}{\gamma}\left(\frac{k_1 + k_2}{k_1} + \frac{k_3}{k_1}\frac{C_N}{C_A}\right). \qquad (1)$$

Here ε_0 and ε_e are the values of the absorption coefficient in the absence of the foreign gas and in the presence of the foreign gas with concentration C_A, respectively; C_N is the concentration of the substance under study; k_1, k_2 and k_3 are the velocity constants of the following reactions:

$$\begin{aligned}
&\text{(I)} \quad N + A \xrightarrow{k_1} N^\wedge + A, \\
&\text{(II)} \quad N^\wedge + A \xrightarrow{k_2} N + A, \\
&\text{(III)} \begin{cases} N^\wedge + N \xrightarrow{k_3} N + N, \\ N^\wedge + N^\wedge \xrightarrow{k_3} N^\wedge + N. \end{cases}
\end{aligned} \qquad (2)$$

The quantity γ is defined as $\gamma = 1 - \varepsilon'^\wedge/\varepsilon$, where ε and $\varepsilon'^\wedge$ are the values of the absorption coefficient for the unperturbed form N and the perturbed form $N^\wedge$ of the molecule under study. Already in reference 1 and in the later investigations it was observed that the molecules of the substances under study can interact among themselves and inhibit the action of the light gases on them.

In reference 4 it was proposed that for the formal description of these interactions a dependence of γ on C_N should be used. It is more expedient, however, to introduce a coefficient $\delta \leqslant 1$ showing the effective fraction of the molecules under study which are not in a state of interaction which prevents them from performing the transition into the perturbed state $N^\wedge$ in a collision with a helium atom. This coefficient obviously enters as a multiplier of the constant k_1 of the reaction I. Expression (1) then takes the form

$$\frac{\varepsilon_0}{\varepsilon_0 - \varepsilon_e} = \frac{1}{\gamma}\left(\frac{\delta k_1 + k_2}{\delta k_1} + \frac{k_3}{\delta k_1}\cdot\frac{Z_N}{Z}\right) \qquad (3a)$$

or, in the units of measurement assumed in the present investigation,

$$\frac{F_0}{F_0 - F_z} = R + Q\frac{Z_N}{Z}, \qquad (3b)$$

where R and Q are constants which can be evaluated by an analysis of the straight lines in Fig. 2. It is clear that

$$R = \frac{F_0}{F_0 - F_\infty} = \frac{\delta k_1 + k_2}{\gamma \delta k_1}, \qquad (4)$$

$$Q = \frac{k_3}{\gamma \delta k_1}. \qquad (5)$$

Here F_∞ is the value of the relative intensity of the fluorescence as $Z \to \infty$; Z_N and Z are the numbers of collisions of the molecules under study with themselves and with atoms of the foreign gas, respectively.

It should be noted that the constants k_1, k_2, and k_3 in expressions (3a), (3b), (4), and (5) refer to a single collision, and not to unit concentration of the gases as in expression (1).

The adequate fulfillment of a linear relationship between $F_0/(F_0 - F_z)$ and $1/Z$, as shown in Fig. 2, indicates that it is possible to apply expression (3) to the experimental data.

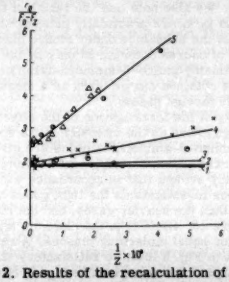

Fig. 2. Results of the recalculation of the experimental data in Fig. 1 by formula (1). The straight lines 1—5 correspond to the curves 1—5 in Fig. 1; the designations are the same.

The unknown quantity γ, for the determination of which the experimental data does not suffice for the time being, is assumed in the following to be equal to unity (the basis for this assumption is given in reference 4). In every case the ratio $\varepsilon'^\wedge/\varepsilon$ remains unchanged at constant temperature; thus the data which we have obtained under all conditions are correct except for a constant factor which probably does not differ greatly from unity (cf. reference 4). The value of R found from the experimental data with this assumption remains constant at very low concentrations of the substance under study (Fig. 2), and then increases with increasing concentration; this must be ascribed to a decrease in the value of δ as a consequence of the appearance of the inhibiting interactions mentioned above. The values of γ determined in this way (at the lowest concentrations clearly $\gamma = 1$) are given along with other data in Table 1.

Using the values of δ it is easy to determine the ratio of the constants, k_1/k_2, and then, taking into consideration the value of the slope of the straight lines in Fig. 2, the ratio of the constants k_1/k_3, also. In connection with the calculated results given in Table 1 it should be noted that the data on the ratio k_1/k_3 for the lowest vapor pressures of the substance under study are very

Table 1. Values of the Constants in Expressions (3)-(5) which Characterize the Effect of Helium as a Function of the Vapor Pressure of 3-Dimethylamino-6-Aminophthalimide

$P_N \times 10^3$ mm Hg	R	δ	$\frac{k_1}{k_3} \times 10^3$	$\frac{k_2}{k_3} \times 10^3$
9.1	1.78	1	(2.35)	(1.82)
23.4	1.78	1	(6.07)	(4.72)
54	1.80	0.98	2.6	2.02
245	1.90	0.87	2.09	1.63
930	2.37	0.57	3.16	2.47

approximate, since from the existing experimental results it is very difficult to obtain reliable values of the slopes of the straight lines in Fig. 2. A sharp decrease in the intensity of the spectra in these cases takes place at pressures of helium so low (Fig. 1) that they could not be used in our measurements.

A consideration of the data obtained shows that the value found here for the limiting concentration, $2\text{-}3 \times 10^{-3}$ mm Hg, below which interaction between molecules of 3-dimethylamino-6-aminophthalimide is practically nonexistent, agrees with the value determined independently in reference 8. We also note that the ratios of the constants k_1/k_3 and k_2/k_3 are practically independent of the concentration of the substance under study. Since the constant k_3 is of course determined only by the properties of the 3-dimethylamino-6-aminophthalimide molecule, the ratios obtained can be taken as a measure of the effect of the foreign gases.

The results of the investigation of the effect of the different foreign gases on the intensity of the spectrum of 3-dimethylamino-6-aminophthalimide are given in Fig. 3 for the rare gases, diatomic, and triatomic gases. It is immediately evident that in accordance with the results of previous investigations the light gases have a greater effect than the heavier gases, and the monatomic gases have a greater effect than the diatomic and triatomic gases for equal molecular masses. A recalculation of the data in Fig. 3 leads to satisfactory straight-line relationships of the type given in Fig. 2, from which the values of the constants k_1/k_3 and k_2/k_3 are obtained; the latter are given in Table 2. All of these experiments were carried out with the 3-dimethylamino-6-aminophthalimide vapor pressure equal to 5.4×10^{-3} mm Hg. Consequently, in the calculations the correction $\delta = 0.98$ was introduced and it was assumed that $\gamma = 1$.

We note that the values of F_∞/F_0, reached with the addition of sufficiently large quantities of the foreign gases ($Z > 10^9$ collisions/sec), practically coincide with the values determined by extrapolation of the straight lines of the type shown in Fig. 2. Consequently we could use also our data on the effect of the hydrocarbon gases, oxygen, nitric oxide, and ammonia, which were added to the 3-dimethylamino-6-aminophthalimide vapor in quantities corresponding to $Z > 10^9$ collisions/sec, without investigating the whole curve of the dependence of F_s/F_0 on Z. On the basis of these data calculated values of the ratio of the constants k_1/k_3 are also given in Table 2 for oxygen, nitric oxide, ammonia, and the hydrocarbon gases.

Table 2. Values of the Ratios of the Constants in Expressions (3)-(5) for 3-Dimethylamino-6-Aminoph phthalimide for Various Kinds of Foreign Gas

Gas or vapor	$\frac{F_\infty}{F_0}$	$\frac{k_1}{k_3}$	$\frac{k_1}{k_3} \cdot 10^3$	$\frac{k_2}{k_3} \cdot 10^3$	Van der Waals interaction constant $a\left(\frac{P \times atm}{cc}\right)$ from ref. 11
He	0.45	1.29	2.6	2.02	0.03
Ne	0.70	0.44	1.08	2.45	0.21
Ar	0.84	0.20	0.40	2.0	1.35
Kr	0.86	0.17	0.37	2.15	2.32
Xe	0.91	0.11	0.20	1.80	4.19
H_2	0.59	6.73	1.04	1.43	0.24
D_2	0.65	0.55	1.00	1.80	0.24*
N_2	0.80	0.26	0.58	2.25	1.39
CO	0.90	0.13	0.23	1.82	1.49
HCl	0.87	0.15	0.31	2.02	5.48
D_2O	0.84	0.21	0.50	2.34	5.46*
O_2	0.87	0.15	—	—	1.36
NO	0.90	0.11	—	—	1.34
NH_3	0.95	0.05	—	—	4.17
C_2H_4	0.90	0.11	—	—	4.47
C_2H_6	0.92	0.09	—	—	8.38
C_3H_8	0.95	0.05	—	—	8.66
C_4H_{10} нор.	0.88	0.14	—	—	14.47
нор.-C_5H_{12}	0.97	0.03	—	—	18.05

*Approximate values corresponding to H_2 and H_2O.

Of the results given in Table 2 the ratios of the constants k_1/k_3 and k_2/k_3 are of the greatest interest; if it is taken into consideration that the value of k_3 is independent of the kind of foreign gas, these ratios are proportional to the probability of the transition from the normal state N into the perturbed state N^ and of the re-

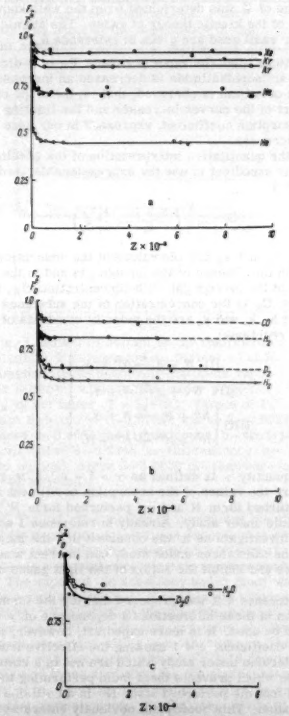

Fig. 3. Effect of foreign gases on the fluorescence intensity of 3-dimethylamino-6-aminophthalimide vapor ($P_N = 5.4 \times 10^{-3}$ mm Hg; T = 528°K). Curve a—rare gases, curve b—diatomic gases, curve c—light and heavy water vapors.

verse transition of the molecule under study when it collides with the foreign particle. It is easy to see that the foreign gases differ only slightly in their ability to initiate the transition $N^{\wedge} \rightarrow N$ on collision with a perturbed molecule $N^{\wedge}$ (approximate equality of the values of k_2/k_3 for the different gases). On the other hand, the foreign gases differ sharply in their ability to produce the transition $N \rightarrow N^{\wedge}$, this ability (k_1/k_3) decreasing as the mass and complexity of the foreign gas molecule increases.

In the previous investigations (cf. reference 9) the suggestion was made that the perturbed state $N^{\wedge}$ differs from the normal state N by a disturbance of the configuration of the π-electron system of the molecule, the two states being separated by a potential barrier due presumably to some structural reorganization of the molecule. The probability of the transition $N + A \rightarrow N^{\wedge} + A$, which is determined first of all by energy relationships (height of the potential barrier), possibly also depends on the momentum relationships of the particles,[10] and evidently requires a definite direction and position for the impact of the foreign gas particle on a "vulnerable" part of the molecule under study. This last condition also explains the special role of the light gases, the molecules of which are less subject to the effect of the Van der Waals force field of the substance being studied which changes the direction and the position of the impact and produces a prolongation of the collision, that is, destroys its "impact" character. In this connection, it has already been suggested in reference 1 that the effect of foreign gases should be determined by the values of the Van der Waals interaction constants for their molecules.

The results obtained by us confirm this point of view. The dependence found for the relative values of the constant k_1 (or k_1/k_3), which govern the process I in Eq. (2), on the Van der Waals interaction constants of the foreign gas molecules* is given in Fig. 4; the points for widely different foreign gases all fall close to a monotonic curve.*

*The values assumed for the Van der Waals interaction constants a are given along with the other data in Table 2.

*If the average value of the ratio of the constants k_2/k_3 obtained from the measurements of the other gases is carried over to oxygen, nitric oxide, ammonia, and the hydrocarbon gases (Table 2) and then the ratio of the constants k_1/k_2 for these gases is calculated, it is easy to show that the values obtained for O_2, NO, NH_3, and the hydrocarbon gases agree satisfactorily with the curve in Fig. 4.

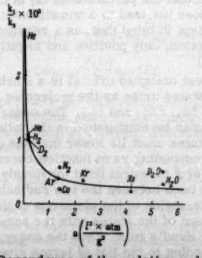

Fig. 4. Dependence of the relative values of the constant k_1 (or k_1/k_3) on the Van der Waals interaction constants of the foreign gas molecules.

We have not been able to find any other characteristic of these molecules which might be correlated with the values of k_1/k_3 in a general monotonic relationship. In particular, the value of the molecular momentum of the foreign gas apparently does not appear as the quantity governing the process; this is indicated by data given in reference 5.

We draw special attention to the fact that for a process involving the transfer of vibrational energy in molecular collisions, in which it is necessary to have the closest and longest possible contact between the colliding particles, a dependence of the opposite kind must occur: the efficiency of energy transfer must increase with an increase in the Van der Waals interaction constant. A dependence of this kind was established by us[9] for these same substances which have been studied in the present investigation.

The fact that the constant k_2 (or k_2/k_3) is practically independent of the type of foreign gas molecule shows that for the transition $N^{\wedge} \rightarrow N$ it is only necessary that there be a collision with any kind of particle; this apparently permits the structural reorganization of the molecule to take place. It is quite evident that with respect to the occurrence of the process $N^{\wedge} \rightarrow N$ collisions of the molecules under study with one another are an order of magnitude more effective than collisions with other particles. From this it follows that either there are factors present which decrease the probability of occurrence of process II in Eqs. (2) to the same extent for all foreign gas molecules, or, the effective radii for the processes III of Eqs. (3) are considerably greater than the gas kinetic radii. Neither of these hypotheses can be excluded. We note that the interaction of the molecules of the substance under study with one another, which we have formally described as a bimolecular process, can be extremely effective, since it has a nature common to the inhibiting (as compared with the effect of foreign gases) interactions of these molecules, which play a significant role at large distances as is evident in particular from the results given in Table 1.

L. I. Shpiller, a student in course V of the Leningrad State University, assisted us in the measurements.

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NONADIABATIC VIBRATIONAL EXCITATION OF MOLECULES DURING MOLECULAR COLLISIONS

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The nonadiabatic vibrational excitation of diatomic radicals during gas-kinetic collisions is considered. It is shown that allowance for the nonadiabaticity, which is substantial when a degenerate electronic state is present in the radical, may lead to a considerable increase in the cross section for vibrational excitation. An estimate of the cross section for the vibrational deactivation of NO corresponds to the experimental results obtained by the method of ultrasonic dispersion and by the optical method in shock waves.

The probability of vibrational excitation of molecules during collisions is generally computed in the adiabatic approximation. In this approximation, it is assumed that at the moment of collision no change takes place in the electronic configuration of the colliding molecules. Calculations of this sort give relatively satisfactory results for many molecules (see, for example, reference 1). However, there exists a large number of cases where the experimental excitation cross sections exceed the theoretical by several orders of magnitude. Among these cases belong, first of all, the collisions of electronically excited molecules and radicals. It is well known that such particles not only are characterized by large cross sections for vibrational excitation, but also enter relatively easily into chemical reaction (see reference 1, p. 322). Attempts to explain the large cross sections by means of a strong attraction of the colliding molecules[2, 3] do not lead to success in some cases, since in such attempts one must assume a very great depth for the potential well.

In the present work it is shown that taking account of the nonadiabaticity of vibrational excitation during a collision of molecules with incompletely filled or excited electron shells may lead to cross sections which considerably exceed the cross sections for adiabatic excitation. The physical picture of an inelastic collision consists of the following. If even one of the colliding partners has a singly occupied orbital, then, during a collision, electronic transitions are possible between the states arising from the initial state, which is degenerate at infinite separation of the molecules. Under the condition that the frequencies of the electronic transition and of the vibrations of the nuclei are equal, there arises a peculiar resonance which brings about a relatively large cross section for the excitation of vibrations.

If we use the adiabatic approximation as a zero-order approximation, the complete wave function of the colliding molecules may be written down in the form

$$\Psi = \psi_l(r,\ R,\ \rho)\varphi_{lv}(R,\ \rho)\chi_{lvt}(\rho), \qquad (1)$$

where ψ_l is the electronic wave function and φ_{lv} and χ_{lvt} are the wave functions of the nuclei for vibrational and relative translational motion. Here r is the set of electronic coordinates; R and ρ are the sets of Jacobian coordinates of the nuclei, referring to vibrations and to translational motion respectively; l, v, and t are the corresponding quantum numbers. The perturbation leading to nonadiabatic transitions has the form

$$\hat{V} = \hat{T}^{el}_{nb} + \hat{T}^{nb}_{\nu} + \hat{T}^{nl}_{\nu} + \hat{A}, \qquad (2)$$

where, for example, $\hat{T}^{el}_{l1b}$ is the operator for the vibrational kinetic energy acting on the electronic wave function, and $\hat{A}$ is the operator for spin-orbital interaction. The term $T^{l1b}_{ll'}$, the matrix elements of which are different from zero only for $l = l'$, governs transitions between vibrational levels of the colliding molecules without change in the electronic state. It is easy to show, following reference 4, that this term leads to the general formulas of the method of distorted waves, which has been developed in its application to molecular collisions by a number of authors (see, for example, reference 2). The remaining terms in (2) may in principle lead, in the first approximation, to a change in the electronic state. However, the probability of such transitions can be significant only in the case where the above-mentioned resonance is realized.

In order to clarify the essential pecularities of the nonadiabatic vibrational excitation of molecules during collisions, let us consider, as a model, the collinear collision of two identical diatomic radicals. Let us assume that there is one electron in the outer orbital of the radical, and that the influence of all the other electrons may be taken into account by the introduction of some self-consistent field. Since we are confining ourselves to the case of a linear collision, we may make use of the classification of electronic states for diatomic molecules.

If the unpaired electron of the radical is in a σ state, then two states—$^1\Sigma^+_g$ and $^3\Sigma^+_u$—arise as the two radicals approach each other. The indices g and u for an even and odd state here characterize the symmetry relative to interchange of the two identical molecular frameworks described by identical self-consistent fields. It is easy to see that, according to the well-known selection rules, the matrix element of $\hat{V}$ between these two states will equal zero, so that the perturbation (2) in the first approximation does not lead to a nonadiabatic transition. (It should be kept in mind that, as a result of the spin-orbital interaction, only positive and negative Σ terms will combine.)

If the lowest occupied orbital is a π orbital, then the following states arise as the molecules approach: $^3\Sigma^-_g$, $^1\Delta_g$, $^1\Sigma^+_g$, $^3\Delta_u$, $^3\Sigma^+_u$, and $^1\Sigma^-_u$. The order in which they are arranged may be established in the following way. All the even states must lie lower than the odd ones, since the corresponding wave function corresponds to the formation of a chemical bond (obviously, the actual formation of a bond between the two radicals depends also on the interaction of the electrons of the framework). The arrangement of the states with the same parity is determined by Hund's rule. Thus the energy levels are arranged according to the list of terms given above.

Since, in the $\hat{T}$ operators for the excitation of vibrations, only the differentiation of the electronic function with respect to R (R is the internuclear distance) is significant, the selection rules for the matrix elements of T read $\Delta\Lambda = 0$, $\Delta S = 0$, $g \rightarrow g$, and $u \rightarrow u$. Then

only Σ^+ and Σ^- terms of different multiplicity and the same parity may combine as a result of the perturbation (2), while it appears that, when the above-mentioned selection rules are taken into account, only the operator for spin-orbital interaction actually emerges as a perturbation. In this case the expression

$$P = \frac{2\pi}{\hbar} \left| \langle lv | \hat{A} | l'v' \rangle \right|^2, \tag{3}$$

where l and l′ correspond to the terms $^3\Sigma_g^+$ and $^1\Sigma_g^-$ or $^3\Sigma_u^-$ and $^1\Sigma_u^+$, is correct for the probability of a nonadiabatic vibrational excitation. The wave function of the relative motion of the initial state must be normalized to unit incident flow, and the final one to a δ function of the energy. Neglecting the dependence of the spin-orbital interaction constant on the vibrational coordinate, we may write expression (3) in the form

$$P = \frac{2\pi}{\hbar} \left| \alpha | A(l, l') B(l, l', v, v') | l' \right|^2, \tag{4}$$

where

$$B(l, l', v, v') = \int \varphi_{lv}^*(R, \rho) \varphi_{l'v'}(R, \rho) \, dR.$$

In order to calculate the probability of excitation of the lower vibrational levels, where the amplitude of the vibrations, $x = R - R_1$, is small in comparison with the radius of action of the exchange forces, $1/\alpha$, the latter integral may be evaluated in the following way. The wave functions $\varphi_{lv}(R, \rho)$ satisfy the equation

$$\hat{T}\varphi_{lv} + U_l(R, \rho)\varphi_{lv} = E_{lv}\varphi_{lv}, \tag{5}$$

in which the dependence of $\varphi_{lv}(R, \rho)$ on l and ρ may be determined to a first approximation by perturbation theory, if we introduce the perturbation operator

$$W_l(\rho, R) = U_l(R, \rho) - U(R, \infty),$$

where U(R, ∞) is the potential of the isolated molecule. Then

$$\varphi_{lv}(R, \rho) = \varphi_v(R) + \sum_{v'} \frac{\langle v' | W_l(\rho, R) | v \rangle}{E_v - E_{v'}} \varphi_{v'}, \tag{6}$$

where $\varphi_v(R)$ satisfies the equation

$$\hat{T}\varphi_v + U(R, \infty)\varphi_v = E_v\varphi_v. \tag{7}$$

Assuming the vibrations to be harmonic and approximating the potential of the intermolecular interaction by an exponential function with the radius of action $1/\alpha$, we find from (6) in the usual way[3]

$$\varphi_{lv}(R, \rho) = \varphi_v(R) + (\alpha x)_{v, v-1} \frac{V_l(\rho)}{\hbar\omega} \varphi_{v-1}(R)$$

$$- (\alpha x)_{v, v+1} \frac{V_l(\rho)}{\hbar\omega} \varphi_{v+1}(R), \tag{8}$$

where $V_l(\rho)$ represents the interaction energy of the radicals in the electronic state l. An analogous expression is also obtained for $\varphi_{l'v'}(R, \rho)$. Substituting (8) in B(l, l′, v, v′), we find

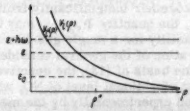
$$B(l, l', v, v') = \frac{(\alpha x)_{v'} |V_l(\rho) - V_{l'}(\rho)|}{\hbar\omega}. \tag{9}$$

Evaluation of a matrix element of (4) on the basis of the wave functions of the relative motion may be carried out in the following way. Since the fundamental contribution to the integral takes place in the immediate neighborhood of the point of resonance ρ^*, which is determined by the condition $\hbar\omega = V_{l'}(\rho^*) - V_l(\rho^*)$ (see Figure), we may approximate the wave functions near that point by Airy functions and we may take the slowly varying integrand function A(l, l′)B(l, l′, v, v′) out from under the integral sign at that point. The corresponding calculation gives (see reference 5, p. 360)

$$P = \frac{|A(l, l')B(l, l', v, v')|^2 \, 4\pi (2\mu)^{1/2}}{\hbar^{1/3}(F_l F_{l'})^{1/3} |F_l - F_{l'}|^{1/2}}$$

$$\times \Phi^2 \left[-(\varepsilon - \varepsilon_0) \left(\frac{2\mu}{\hbar^2} \right)^{1/3} \left(\frac{1}{F_l} - \frac{1}{F_{l'}} \right)^{1/3} \right], \tag{10}$$

where the forces F_l and $F_{l'}$ are evaluated at the point of resonance ρ^* and Φ denotes the Airy function. The quantity ε_0 corresponds here to the greater of the quantities V_l or $V_{l'}$ in the case of excitation, and to the lesser in the case of deactivation, while ε denotes the kinetic energy of the colliding molecules at infinity. For the sake of concreteness, we shall consider deactivation and shall suppose that $V_l > V_{l'}$. Then in our case l corresponds to the term $^1\Sigma_g^-$ and l′ to the term $^3\Sigma_g^+$. Correspondingly, we get $F_l = (\varepsilon_0 + \hbar\omega)\alpha$ and $F_{l'} = \varepsilon_0\alpha$.



The radius of action of the exchange forces, $1/\alpha$, may be approximately determined from the Morse potential for diatomic molecules. The quantity α is connected with the vibrational frequency ω and the dissociation energy D by the relationship $\omega = \alpha\sqrt{2D/m}$, while α maintains for different molecules the approximately constant value 2×10^8 cm^{-1}. Taking into account that the number of quanta n of a Morse oscillator equals $2D/\hbar\omega$, we shall hereafter set $\alpha^2 = m\omega/\hbar n$. Then expression (10) takes the form

$$P_{v, v-1} = v \, |(\alpha x)_{10}|^2 \, A^2 4\pi \, \frac{\varepsilon_0 + \hbar\omega}{\varepsilon_0 (\hbar\omega)^2} \gamma^2 \Phi^2 \left(-\frac{\varepsilon - \varepsilon_0}{\varepsilon_0} \gamma \right), \tag{11}$$

where the abbreviated symbol

$$\gamma = \left[\frac{2\mu x \hbar\omega \varepsilon_0}{m(\varepsilon_0 + \hbar\omega)^2} \right]^{1/3}$$

has been introduced. From the asymptotic behavior of Φ(x), it follows[5] that for positive arguments of the Airy function the probability diminishes exponentially, while for large negative arguments it oscillates rapidly. In the latter case expression (11) goes over into the Landau-Ziner formula

$$P_{v, v-1} = v \, |(\alpha x)_{10}|^2 \frac{4\pi A^2}{\hbar \sqrt{\frac{2(\varepsilon - \varepsilon_0)}{\mu} |F_l - F_{l'}|}}. \tag{12}$$

Averaging of the probability over the thermal distribution of the colliding molecules may be approximately carried out thus. If $kT \geq \varepsilon_0$, then ε may be replaced in (12) by $\bar{\varepsilon}$. Under the condition $kT < \varepsilon_0$, it is necessary to use formula (11). Since $\Phi^2(x)$ near $x = 0$ changes substantially in an interval of the order of unity, we may consider the deactivation probability to be different from zero only in the case where the relative energy of the colliding molecules lies close to ε_0 and is included in the energy interval $\varepsilon - \varepsilon_0 \approx \varepsilon_0/\gamma$. In this way we obtain from (11)

$$P_{v, v-1} = v \, |(\alpha x)_{10}|^2 \, A^2 4\pi \, \frac{\varepsilon_0 + \hbar\omega}{kT(\hbar\omega)^2} \gamma \exp\left(-\frac{\varepsilon_0}{kT} \right). \tag{13}$$

The probability $P_{v, v-1}$ calculated according to formulas (12) or (13) corresponds to the transition of two colliding molecules from one potential curve to another. To obtain the total probability, it is necessary to average

over the initial electronic states and to sum over the final ones, taking account of degeneracy with respect to the projections of the spins and moments. Such an averaging leads to the appearance in (13) of a factor $g < 1$.

For nonlinear collisions of the radicals, the considerations presented above concerning the selection rules in the combination of electronic states become incorrect. Since, however, the operator for spin-orbital coupling does not depend critically on the mutual orientation of the radicals at the moment of collision, and the deviation from a collinear configuration leads to the appearance of new transitions which were previously forbidden by virtue of the axial symmetry, we may expect that the probability of a real three-dimensional collision may change somewhat, but that with respect to order of magnitude it must still be determined by expression (13). Strictly speaking, expression (13) gives the probability of vibrational excitation while passing twice through the point of resonance ρ^*. Since, however, ρ^* in our approximation differs altogether insignificantly from the gas-kinetic radius ρ_0, the quantity $P_{v,\,v-1}$ may be considered as the probability for a single gas-kinetic collision.

As an illustration of the general considerations, let us estimate, on the basis of (13), the deactivation probability of the first vibrational level of NO, which was recently measured experimentally by the method of ultrasonic dispersion[6] and by the optical method in shock waves.[7] The basic difficulty lies in the estimation of ε_0, since it is impossible to calculate the terms of such a complex system with the necessary accuracy. However, the value of ε_0 may be very roughly estimated in the following way. The splitting ΔV between the $^1\Sigma^+$ and $^3\Sigma^-$ terms of the 2NO system is controlled only by the exchange interaction of the two π-electrons. This interaction diminishes exponentially for weak overlapping of the electron shells, so that one may write, as an approximation,

$$\Delta V(\rho) \simeq \Delta V_0 \exp[-\alpha(\rho - R_e)], \tag{14}$$

where R_e is the equilibrium internuclear distance in the NO molecule. The quantity ΔV_0, which characterizes the splitting for strong overlapping of the wave functions, must be of the order of 1 or 2 ev. (The corresponding splitting in the O_2 molecule, which likewise contains two π-electrons in its outer orbital, equals 1.6 ev.)

On the other hand, the energy of the intermolecular interaction must be approximated by a potential of this form:

$$V(\rho) = C \exp(-\alpha\rho), \tag{15}$$

where the constant C may be determined, for example, from the gas-kinetic radius ρ_0 by the condition $V(\rho_0) \simeq kT_0$, where T_0 corresponds to the temperature at which the value of ρ_0 was determined. Combining (14) and (15), we find

$$\varepsilon_0 = V(\rho^*) \simeq \frac{\hbar\omega \cdot kT_0}{\Delta V_0} \exp[\alpha(\rho_0 - R_e)]. \tag{15a}$$

Supposing here $\alpha = 2 \times 10^8$ cm^{-1}, $\omega = 2000$ cm^{-1}, $T_0 = 300°$, $\Delta V_0 = 1$–2 ev, $R_e = 1.1$ A, and $\rho_0 \simeq 3$ A (the average van der Waals radius for all six electronic states equals 3.6 A, but the equilibrium distance in the dimer $(NO)_2$ in the liquid phase equals 2.4 A), we find $\varepsilon_0/k \simeq 1000$–$2000°$K. Such an energy value leads, according to (13), to a weak positive temperature dependence of the deactivation probability for $T \leq 1000$–$2000°$K. This conclusion corresponds qualitatively with the experimental results of reference 7, in which it was found that the deactivation probability increases only fourfold altogether when the temperature is increased from 500 to 1000°K. This very circumstance—the weak temperature dependence of $P_{1,0}$—gives evidence of the inapplicability in this case of the Landau-Teller formula, according to which the experimental results were worked out in reference 7. We note that a temperature dependence of the Landau-Teller type, which is correct for adiabatic deactivation, would lead (when the radius of action is properly chosen) to a hundred-fold change in cross section in this temperature interval.

For an estimate of the numerical value of $P_{1,0}$, let us suppose $|(\alpha x)_{10}|^2 \simeq 10^{-2}$, $A = 100$–200 cm^{-1} (the spin-orbital splitting in the NO molecule amounts to 120 cm^{-1}, and in the O_2^+ ion to 200 cm^{-1}),* $\omega = 2000$ cm^{-1}, $m = \mu/2$, $n \simeq 10^{19}$, $T = 500°$K. The quantity g for a collinear collision equals 3/16, but for other configurations it may exceed this value. Substituting these values in (13), we obtain $P_{1,0} \simeq 10^{-4}$. The experimental value of the quantity $P_{1,0}$ at this temperature[7] equals 7×10^{-4}. A calculation of the cross section made under the assumption of adiabaticity[8] would lead to the value 10^{-8}.

*Kovacs' works[9] are devoted to an exact evaluation of the matrix elements of the operator for spin-orbital interaction in diatomic molecules.

Thus the mechanism of nonadiabatic excitation enables us to give an intelligent explanation of the large difference in the vibrational excitation cross sections of the NO radical and the O_2 and N_2 molecules, which has been noted by a number of authors.[6, 7]

As for vibrational relaxation in a system of NO radicals, it must be subject to the rules for relaxation of weakly anharmonic oscillators, as considered in reference 8. This follows from the fact that the deactivation probability $P_{1,0}$ depends relatively weakly on the magnitude of the vibrational quantum $\hbar\omega$.

Apparently the mechanism of nonadiabatic relaxation may also explain the very large deactivation probabilities obtained in the work of Kleinberg and Terenin[10] for the NO radical in the excited $A^2\Sigma^+$ state. In this case it is necessary to take into account the interaction of the closely-spaced excited states $A^2\Sigma^+$, $B^2\Pi$, and $^4\Pi$; however, it is no longer possible to choose the ratio of the amplitude of the vibrations to the radius of action of the exchange forces as a small parameter which characterizes the perturbation. This is connected with the circumstance that the essential change in the electronic state takes place, during the excitation of the lower vibrational levels of the $A^2\Sigma^+$ state, as a result of the intersection of the potential curves, so that the zero-order adiabatic approximation, which leads to low values of the deactivation probability, becomes inapplicable. The interaction between the electronic states indicated above manifests itself optically in well-known anomalies of the NO spectrum.[11]

Recently Roth[12] investigated the emission spectrum of CN in shock waves. On the basis of the intensity distribution, a vibrational relaxation time was determined, corresponding probably to the transition $v' = 1 \rightarrow v' = 0$ in the excited electronic state $B^2\Sigma^+$. The absolute magnitude of the cross section was not determined, but it was found that the temperature dependence of the cross section follows the Landau-Teller formula with the anticipated value for the radius of action of the exchange forces, 0.46–0.44 A. The theoretical conclusions which we have reached concerning the impossibility of nonadiabatic relaxation of radicals in the $^2\Sigma$ state agree with the experiment in this case also.

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AN OPTICO-ACOUSTIC PHENOMENON IN THE VISUAL AND ULTRAVIOLET SPECTRAL REGIONS AND ITS RELATION TO THE PHOTOCHEMICAL PROCESSES IN GASES

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An optico-acoustic effect was observed in the near ultraviolet in chlorine, and in the visible spectrum region in nitrogen dioxide by means of an apparatus which was assembled from parts of a standard optico-acoustic gas analyzer, and which contained sources of ultraviolet radiation. The gas characteristics of the optico-acoustic gas analyzer for chlorine were obtained.

A sharp intensification of the optico-acoustic effect was found when hydrogen was introduced into the optico-acoustic chamber containing chlorine; the intensification is apparently caused by production of an additional optico-acoustic effect during a photochemical reaction between chlorine and hydrogen.

The optico-acoustic effect was known up to the present time only in the infrared spectrum region. Gerlovin[1] reported recently an optico-acoustic effect observed by him in the ultraviolet in nitrogen, oxygen, and acetylene. The observation of the optico-acoustic effect outside the infrared is interesting, because the optico-acoustic method thus becomes applicable to gases, which do not absorb the infrared radiation (oxygen, hydrogen, chlorine, etc.). Furthermore, this effect is important from a theoretical standpoint, inasmuch as the mechanism of the optico-acoustic phenomenon in the ultraviolet and visible spectral regions differs from that of the mechanism in the infrared region. While this effect is produced in the infrared by the increase of the translational energy of the molecules due to absorption of the radiant energy by the gas, in the ultraviolet and visible regions a substantial part might be caused also by the dissociation of molecules during irradiation.

For observation of the phenomenon in the ultraviolet and the visible regions of the spectrum a set-up was used which is shown in Fig. 1. Radiation fluxes from sources 1 are modulated by the chopper 2 with the frequency 6 cps and pass through the light filters 4, and then through the absorption cell 5, through which the gas under investigation is flowing, and through the comparison cell 6 not containing the gas, respectively.

In front of the cells are light filters 4 which select the needed spectral region, and shields 3 for equalizing the radiation fluxes.

Both radiation fluxes, modulated in the same phase, enter the radiation receivers of the measuring (optico-acoustic) chamber 7 filled with the gas under investigation. A membrane of a condenser microphone divides the measuring chamber in two equal parts causing the microphone to react to the difference in the changeable pressures appearing in the two radiation receivers. The microphone of the optico-acoustic chamber is connected through the cathode follower 8 to the input of the amplifier 9, to the output of which a vacuum tube voltmeter and an electronic oscillograph 10 are connected. The sensitivity of the microphone outside the chamber was approximately 12 mv/bar.

The measuring chamber was made of stainless steel. The windows were made of synthetic corundum and tightened with phtoroplast rings. The diameter of the windows was 20 mm.

The lamps UFO and PRK-4 were used as sources of

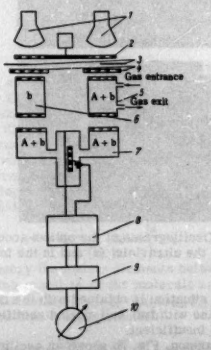

Fig 1. Setup for observation of the optico-acoustic effect in the visible and ultraviolet spectral regions. A—gas to be analyzed; B—nonabsorbing mixture.

ultraviolet radiation. The source of visible light was the incandescent lamp K 7 (12 volts, 30 watts). For transmission of the ultraviolet radiation and blocking the infrared, glass light filters UFS-1 of 3 mm thickness were used.

For the comparison of the optico-acoustic effect in the ultraviolet and in visible spectral regions with that in the infrared, nichrome spirals heated to the temperature of 600 to 650°C and placed in the focal points of parabolic reflectors were used for sources. Germanium plates 1 mm thick were used as filters for the selection of the infrared radiation.

It has been found that by irradiation of the optico-acoustic chamber filled with chlorine, with the lamp UFO, an electromotive force up to 10 mv was generated at the output of the cathode follower (the second optical channel being shielded). When the lamp UFO was substituted by PRK-4 (working at about 20% of the nominal power), the emf generated by the chamber increased to 20 or 25 mv. The ratio of the emf generated by the chamber, to the total electric and acoustic impedance measured at the output of the cathode follower, reaches approximately 50. At the output of the resonance amplifier it can be made as high as several thousand.

It must be taken into consideration that the radiation sources were both of a considerable size, so that losses of a major part of the radiation fluxes emitted by them could not be avoided.

Figure 2a depicts the oscillogram of the emf obtained from the lamp PRK-4. The oscillogram shows a "comb" of a frequency of 100 cps superimposed on the basis modulation frequency of 6 cps due to the modulation of the lamp radiation by the line frequency. Of course, the "comb" disappears during the dark periods. The emf generated by the chamber at the frequency of 100 cps (without the chopper) is about one third of that generated with the frequency 6 cps.

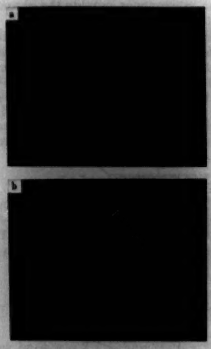

Fig. 2. Oscillograms of the optico-acoustic effect in the ultraviolet (a) and in the infrared (b).

A similar situation is obtained with the lamp UFO fed by the ac line with two-half-period rectification, when the filtering is insufficient.

For comparison, Fig. 2b shows an oscillogram of the optico-acoustic effect produced by the action of the infrared radiation in the absorbing gas.

Figure 3 depicts the gas characteristics (emf vs gas concentration in the absorption cell). Curve a was obtained with the lamp UFO, curve b—with the lamp PRK-4, and curve c with the same lamp and the light filter UFS-1. The length of the absorption cell was 20 mm. For comparison of the results of measurements with different radiation sources, they are given as ratios J of the signal with gas in the absorbing cell, to the signal with a completely closed shield of the working channel.

For investigation of the optico-acoustic effect in the visible region, the measuring chamber was filled with nitrogen dioxide. The emf generated in the chamber with the lamp PRK-4 was found to be insignificant. By using the incandescent lamp K7 there was a considerable optico-acoustic effect. Selection of various spectral ranges of the lamp by means of light filters has demonstrated that the largest part of the emf generated by the chamber is due to the visible spectrum range.

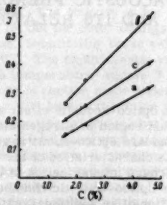

Fig. 3. Dependence of the ratio

$$J = \frac{\text{signal from gas}}{\text{signal from total flux}}$$

in the ultraviolet, on concentration C of chlorine in the absorption cell (gas characteristics). a—with the lamp UFO as source; b—with lamp PRK-4; c—with PRK-4 and filter UFS-1. Length of the cell 20 mm.

In conclusion, mention should be made of a curious effect which is produced when hydrogen is added to chlorine in the optico-acoustic chamber, and a source of ultraviolet radiation is used. It was found that immediately after the introduction of hydrogen the optico-acoustic effect had increased several times, and then gradually decreased in two or three hours to about the original value. Successive additions of the same quantities of hydrogen cause again an increase of the optico-acoustic effect, but to a progressively smaller degree. At the same time, a gradual increase of the optico-acoustic effect in the infrared was observed.*

*In a chamber filled with chlorine an insignificant optico-acoustic effect in the infrared is observed due to admixtures in chlorine and perhaps due also to the non-selective absorption of radiation by the chamber walls.

Several control experiments were made to establish the cause of the described effect. In particular, in order to check whether this effect is caused by the specific action of hydrogen, some air was introduced into the chamber, and this caused a decrease of the optico-acoustic effect (in contradistinction to hydrogen). The absence of the optico-acoustic effect when the chamber is filled with pure hydrogen supports the explanation that this effect is connected with the interaction of chlorine and hydrogen, and not with the optico-acoustic effect from hydrogen; this could be anticipated since the absorption spectrum of hydrogen is in a shorter wavelength region than that emitted by the lamps UFO and PRK-4. Furthermore, it

was found that on introducing some hydrogen in the optico-acoustic chamber with chlorine, a noticeable sensitivity to the vapors of hydrogen chloride in the infrared region was observed, if the latter is made to flow through the absorption chamber. It follows from the last mentioned observation that the presence of the hydrogen chloride can be expected in the optico-acoustic chamber. A qualitative chemical analysis of a gas sample taken from the optico-acoustic chamber did actually show that noticeable quantities of hydrogen chloride were present.*

*It should be noted that the optico-acoustic effect could only decrease, but could not increase, if the hydrogen would remain in the chamber without reacting, because hydrogen has a high heat capacity.

In our opinion, the above described phenomena can be explained by the assumption that during the half-period of illumination some of the chlorine molecules are dissociated into atoms. Under this condition, a photochemical reaction may take place between chlorine and hydrogen during the half-period of illumination in the chamber with the formation of hydrogen chloride, a reaction which ceases during each dark period. The heat energy periodically evolved during this reaction is added to the heat energy evolved during the absorption by chlorine of ultraviolet radiation flux, thus intensifying the optico-acoustic effect. The gradual decrease of this effect with time is caused by the irreversibility of the photochemical reaction, as a result of which the number of the molecules participating in the reaction gradually diminishes. The intensity of the optico-acoustic effect stabilized at the end of the reaction is determined by the absorption of the ultraviolet radiation by the excess of chlorine, inasmuch as the absorption spectrum of hydrogen chloride occurs in a shorter ultraviolet wavelength region of the spectrum than that emitted by the lamps PRK-4 and UFO.

The effect discovered indicates that in the future, the optico-acoustic method is likely to be used in the study of some photochemical problems.

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ON THE INTENSITIES OF RAMAN LINES*

*Translation Editor's note: We hope to include comments on this paper by American workers in an early issue of JOSA.

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Questions connected with the intensities of Raman lines are investigated. Expressions for the intensities, differing from the widely known formulas of Placzek, are derived. The formulas obtained are transformed using the adiabatic approximation. It is shown that the experimental data for two benzene lines agree much better with the theoretical values calculated on the basis of the derived expressions, than with the computations using Placzek's formulas. In addition, the question of the influence of the solvent on the Raman line intensity is examined.

THE GENERAL EXPRESSION FOR THE LIGHT INTENSITY IN RAMAN SCATTERING

In the investigation of Raman line intensities the formulas obtained by Placzek[1,2] are generally used, according to which the intensity of the scattered radiation in gases is defined by the fourth power of the frequency of the scattered radiation and a squared combination of the respective scattering tensor. The formulas are arrived at on solution of the problem of the interaction of light with the substance using the expression for the energy of interaction in the form

$$W' = -\sum_k \mathbf{E}(k)\,\mathbf{M}_k, \qquad (1)$$

where $\mathbf{E}(k)$ is the electric vector of the light wave at the position of the k-th particle, and $\mathbf{M}_k$ is the dipole moment of the k-th particle. Expression (1) is used both for the classical description and for the quantum-mechanical examination of the problem.

It should be noted that expression (1) does not appear to be sufficiently well grounded. Indeed, it is simply carried over from electrostatics which, generally speaking, is not valid. More appropriate is the construction by well-known laws of the complete Hamiltonian of the system of particles and field with subsequent separation of the terms describing the interaction of the field with the substance. For the case where the particle momentum is nonrelativistic, the expression for the interaction has the form[3]

$$W = -\sum_k \frac{e_k}{cm_k}\mathbf{A}(k)\,\mathbf{p}_k + O(A^2). \qquad (2)$$

Here $\mathbf{p}_k = -i\hbar\nabla_k$ is the momentum operator of the k-th particle and A is the vector potential of the wave (taken as the Coulomb potential ($\varphi = \operatorname{div} \mathbf{A} = 0$) in which the field is considered to be weak).

It is not difficult to prove that (1) and (2) generally lead to different results. We shall illustrate this with an example, in which the electromagnetic field is not quantized, but is considered as a classical perturbation field with a time dependence of the type $\mathbf{A} = \mathbf{A}_0 e^{-i\omega t}$. The electrical field in this case has the form

$$\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}, \quad \mathbf{E}_0 = \frac{i\omega}{c}\mathbf{A}_0. \qquad (3)$$

In the theory the matrix elements between certain quantum states n and m of the molecule are essential. Using the relationship $(p_{xk})_{nm} = m_k i\omega_{nm}(x_k)_{nm}$ and Eq. (3) we find (in the dipole approximation)

$$W_{nm} = -\frac{i\omega_{nm}}{\omega}(\mathbf{EM}_{nm}), \quad W'_{nm} = -(\mathbf{EM}_{nm}), \qquad (4)$$

where $\mathbf{M}$ is the dipole moment of the entire molecule. From this it is evident that W_{nm} and W'_{nm} do not coincide,

in general. In a series of particular cases, however, chance coincidence is possible. Thus, for all processes of the first order, coincidence occurs as a result of the fact that for the states participating in the phototransition it is known that $\omega_{jm} = \omega$. In dispersion theory in the calculation of the polarizability tensor α of the molecule as the proportionality coefficient between $\mathbf{M}$ and $\mathbf{E}$, different results are obtained for the nondiagonal matrix elements of α depending on which expression is used for the description of the interaction of light with the substance, while the results for the diagonal elements coincide far from an absorption band. The same expressions are also obtained for the refractive index of light in gases, obtained on the basis of calculations[4,5] with the aid of (1) and (2).

For Raman scattering the correct expression may be strictly obtained only within the limits of quantum electrodynamics. Then the result proves to be different depending on which expression is chosen for the interaction energy of the molecule with the light—form (1) (according to Placzek) or (2). The calculation for the interaction in the form (2) has been carried out, for example, by Heitler.[3] He obtains an expression for the differential effective scattering cross section of a light quantum inside the solid angle $d\Omega$, appearing as the ratio of the transition probability per unit time for absorption of the quantum $\hbar\omega_0$ and radiation into the angle $d\Omega$ of the quantum $\hbar\omega$ (with fixed polarization) to the flux density of the incident quanta. If the above-mentioned transition probability is multiplied by the energy $\hbar\omega$, then we obtain, clearly, the energy radiated into the angle $d\Omega$ in unit time. The flux density of the incident monochromatic photons, multiplied by the photon energy $\hbar\omega_0$, determines the average intensity of the incident light I_0. Therefore, if the right side of the appropriate formula[3] is multiplied by ω/ω_0 and divided by $d\Omega$, then we obtain the ratio of the light intensity I, radiated in a given direction, to the intensity of the incident light I_0. This is

$$I = \left(\frac{\omega}{\omega_0}\right)^3 \left| \sum_j \left[\frac{(S_1)_{mj}(S_0)_{j1}}{\hbar(\omega_{j1} - \omega_0)} + \frac{(S_0)_{mj}(S_1)_{j1}}{\hbar(\omega_{jm} + \omega_0)} \right] \right|^2 I_0. \qquad (5)$$

Here the indexes 1, j, and m denote the initial, intermediate, and final states of the molecule, $\omega_{j1} = (E_j - E_1)/\hbar$, and E_j is the energy of the j-th state. The operator S is defined in the following manner:

$$\mathbf{S} = \sum_k \frac{e_k}{cm_k} \mathbf{p}_k. \qquad (6)$$

and the subscripts 1 and 0 signify the projections on the direction of polarization of the scattered and incident photons, respectively. (The summation is carried out over all states of the molecule.)*

*We note before obtaining (5) from the appropriate Heitler formula that there are several generalizations involved in the latter, since it is written for the case of an atom with one electron and a stationary nucleus. The generalization for the case of a larger number of electrons and nuclei in motion may be carried out without difficulty, and we will not discuss this point any further.

Expression (5) differs significantly from Placzek's formula for the Raman intensity: instead of a proportionality far from an absorption band of ω^4 we have the proportionality factor $(\omega/\omega_0)^3$, which is generally of the order of unity; and, secondly, the matrix elements of the operator S, defined in (6), appear in Eq. (5) instead of the matrix elements of the dipole moment. The constant factor in (5) naturally will also be different.

Relation (5) if desired may be given the more usual form for the radiation of an oscillator with dipole moment of 2P

$$I = \frac{\omega^4}{2\pi c^3} |P_1|^2, \qquad (7)$$

and

$$\mathbf{P} = \alpha \mathbf{E}_0, \quad \alpha_{xy} = \frac{1}{\hbar} \sum_j \frac{\omega_{jm}\omega_{j1}}{\omega\omega_0} \left[\frac{(M_y)_{1j}(M_x)_{jm}}{\omega_{j1} - \omega_0} + \frac{(M_x)_{1j}(M_y)_{jm}}{\omega_{jm} + \omega_0} \right]. \qquad (8)$$

The field is assumed to have in the region of the molecule the form $\mathbf{E} = \mathbf{E}_0 2\cos\omega t$ and $I_0 = (C/2\pi)E_0^2$. Of course, formulas (5) and (7) are completely identical since (7) is only another way of writing (5).

We will call the tensor α given in (8) the Raman tensor. It differs from the commonly derived expression by the presence of the factor $\omega_{j1}\omega_{jm}/\omega\omega_0$ in the sum over j. This factor also leads to a different dependence of I on ω as compared with Placzek's theory.[1,2]

It is natural that all consequences of Placzek's theory, for which the dependence of I on ω is not critical, remain in force. Thus, the formulas defining the indicatrix of the Raman scattering[1,6] are still valid; and, in part, concerning these results, the Placzek theory acquires a firmer foundation.

REARRANGEMENT OF THE RAMAN TENSOR

We will rearrange expression (8) using the adiabatic approximation and define the state of the molecule by two quantum numbers, e.g., (lv), where the first relates to the electronic and the second to the nuclear motions.* We introduce the following symbols: for the energy of the state (lv)—E_v^l,

$$\omega_{v_p}^{jl} = \frac{(E_p^j - E_v^l)}{\hbar};$$

for the matrix elements of the transition between the states (jv_i) and (lv)—$(S_x)_{v_i v}^{jl}$. Then in the case where the molecule goes from the state (lv) into the state (mv′) we have for the tensor (8) the following expression

$$(\alpha_{xy})_{vv'}^{lm} = -\frac{e^2}{\omega\omega_0} \sum_{jp_i} \left[\frac{(S_y)_{mv_i}^{lj}(S_x)_{v_i v}^{jm}}{\hbar(\omega_{v_i v}^{jl} - \omega_0)} + \frac{(S_x)_{mv_i}^{lj}(S_y)_{v_i v}^{jm}}{\hbar(\omega_{v_i v}^{jl} + \omega_0)} \right] \qquad (9)$$

$$\equiv -\frac{e^2}{\omega\omega_0} \left[(a_{xy})_{vv'}^{lm} + (b_{xy})_{vv'}^{lm} \right].$$

The approximate calculation of the tensor, in the theory of Raman scattering, is generally carried out by a simultaneous expansion of the matrix elements (in which the matrix operation is executed only over the electronic coordinates) in a power series over the nuclear coordinates, and of the frequency factors in a power series over the differences between the energies of the arbitrary and of the Frank-Condon transitions.[2] In our case the respective matrix elements have the form

$$S_x^{lj}(Q) = \int \psi_l^*(\xi, Q) S_x \psi_j(\xi, Q)\, d\xi, \qquad (10)$$

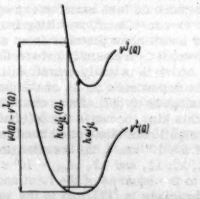
where $\psi_l(\xi, Q)$ and $\psi_j(\xi, Q)$ are the wave functions of the electronic motion, depending on all the electronic coordinates ξ and on the nuclear (normal) coordinates Q (as parameters). We will expand $S_x^{lj}(Q)$ over $Q - Q_l$,

*More accurately, l and v replace the totality of quantum numbers. The state of the rotational motion does not influence the integrated intensity of the scattering.

and S_x^{lm} over $Q - Q_m$ (Q_l and Q_m are the equilibrium positions of the nuclei in the l-th and m-th electronic states). We will expand the frequency factors in a power series of the arguments

$$\frac{\omega_{\nu'\nu}^{lm} - \omega'_{jl}}{\omega'_{jl} - \omega_0} \text{ and } \frac{\omega_{\nu'\nu}^{lm} - \omega'_{jm}}{\omega'_{jm} + \omega_0},$$

in which ω'_{jl} and ω'_{jm} are the frequencies corresponding to the Frank-Condon transition (cf. the Figure). Below we obtain the expression for the general term of the expansion.



It is convenient to first expand the frequency factors, make a few rearrangements, and then to perform the expansion of the quantities $S_x^{lj}(Q)$. We will examine the first component of expression (9)—$(\alpha_{xy})_{\nu'\nu}^{lm}$. After the expansion of the frequency factors we obtain

$$(\alpha_{xy})_{\omega'}^{lm} = \sum_{n=0}^{\infty} [(\alpha_{xy})_{\omega'}^{lm}]_n, \tag{11}$$

$$[(\alpha_{xy})_{\omega'}^{lm}]_n = \frac{(-1)^n}{\hbar} \sum_{j_n} \frac{(S_y)_{n'}^{lj} (S_x)_{n'\nu}^{jm} (\omega_{n'\nu}^{jl} - \omega'_{jl})^n}{(\omega'_{jl} - \omega_0)^{n+1}}. \tag{12}$$

Let us examine the sum over ν in (12). Making use of the property of completeness of the eigenfunctions of the energy operator of the nuclear motion in the j-th electronic state H^j, it is possible to show that

$$\sum_{n_j} (S_y)_{n'}^{lj} (S_x)_{n'\nu}^{jm} (\omega_{n'\nu}^{jl} - \omega'_{jl})^n = \frac{1}{\hbar^n} [S_y^{lj} (H^j - E_\nu^j - \hbar\omega'_{jl})^n S_x^{jm}]_{\nu'\nu}. \tag{13}$$

Further, we expand $S_y^{lj}(Q)$ and $S_x^{jm}(Q)$

$$S_x^{jm}(Q) = \sum_{p=0}^{\infty} (S_x^{jm})_p (Q - Q_m)^p. \tag{14}$$

Turning to the expression for $(\alpha_{xy})_{\nu'\nu}^{lm}$, it is possible, using (13) and (14), to write it in the form

$$(\alpha_{xy})_{\omega'}^{lm} = \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} [(\alpha_{xy})_{\omega'}^{lm}]_{nj}, \tag{15}$$

$$[(\alpha_{xy})_{\omega'}^{lm}]_{nj} = \tag{16}$$

$$\sum_{q+r=0} \sum \frac{(-1)^n (S_y^{lj})_q (S_x^{jm})_r [(Q - Q_l)^q (H^j - E_\nu^j - \hbar\omega'_{jl})^n (Q - Q_m)^r]_{\nu'\nu}}{[\hbar(\omega'_{jl} - \omega_0)]^{n+1}}.$$

The formulas for $(b_{xy})_{\nu'\nu}^{lm}$ also have an analogous form. They are obtained from (15) and (16) by replacing a by b, ω_0 by $-\omega_0$, E_ν^m by $E_{\nu'}^m$, ω'_{jl} by ω'_{jm}, and by permutation of the indexes x and y. These formulas, together with (15) and (16), define the complete tensor

$$(\alpha_{xy})_{\omega'}^{lm} = -\left(\frac{e^2}{\omega\omega_0}\right) \sum_{n=0}^{\infty} [(\alpha_{xy})_{\omega'}^{lm}]_{nr}.$$

We will examine, in more detail, by far the most important case, when $l = m$ and $\nu' = \nu \pm 1$. We will also assume that the tensor α is transformed to its principal axes (this does not restrict the generality of the examination). It is immediately evident that $[(\alpha_x)_{\nu'\nu}^{ll}]_{n0} = 0$. Limiting ourselves to the terms $[(\alpha_x)_{\nu'\nu}^{ll}]_{n1}$ and $[(\alpha_x)_{\nu'\nu}^{ll}]_{n0}$*

*In the examination of $[(\alpha_x)_{\nu'\nu\pm1}^{ll}]_{n0}$ the calculation of $H^j_{\nu'\nu\pm1}$ is required. This quantity equals $(H^j + V^j - V^j)_{\nu'\nu\pm1}$. (V is the potential energy of the nuclear motion.) To obtain (17) it is necessary to neglect the difference between $V^j(Q) - V^l(Q)$ and $\hbar\omega'_{jl}(Q)$ (cf. Figure).

we have

$$(\alpha_{xy})_{\omega\pm1}^{ll} \approx -\frac{e^2}{\hbar\omega\omega_0} \sum_{j(\neq l)}' \left\{ \frac{2\omega'_{jl}}{\omega_{jl}'^2 - \omega_0^2} [(S_x^{lj})_1 (S_y^{jl})_0 + (S_y^{lj})_0 (S_x^{jl})_1] - 2\frac{\omega_{jl}'^2 + \omega_0^2}{(\omega_{jl}'^2 - \omega_0^2)^2} |(S_x^{lj})_0|^2 \left(\frac{\partial\omega'_{jl}(Q)}{\partial Q}\right)_{Q=Q_l} \right\} (Q - Q_l)_{\omega\pm1}. \tag{17}$$

Formula (17) is similar to the corresponding formula of Vol'kenshtein and El'yashevich.[5,7] There is, however, a difference in that the matrix elements of the operator S, given by (6), occur in (17) instead of the matrix elements of the dipole moment, as in the previous work.[5,7] This leads to the necessity of making a more accurate evaluation of the relative roles of both terms occurring under the summation sign in (17) and those presented in reference 2. Not having the opportunity to go into this in more detail, we will only remark that in our opinion these evaluations will also remain valid for the tensor (17), since the matrix elements of the dipole moment and of the momentum are proportional to one another; i.e., in the common cases there will occur in (17) a term containing $[\partial\omega'_{jl}(Q)/\partial Q]_{Q=Q_l}$. Calculations based on experimental data, relating to a concrete instance [cf. below, the benzene case), confirm this assumption.

We also note that our deduction of formula (17) appears to be more general than the deduction of the corresponding formula reported previously.[5,7] Expression (17) is obtained for arbitrary l and (which is of greater significance) ν. In addition, we do not depend on the specific form of the functions describing the nuclear motion. The single requirement which was used was the completeness of the system of eigenfunctions of the operator H^j.

Formulas for the arbitrary term of the expansion of the tensor α are first obtained. Practically, their application is currently limited by the fact that we do not know the electronic wave functions of the molecule and, accordingly, also the parameters $(S_y^{lj})p$ (cf. (16)). A method in which these quantities were determined from the experimental data would evidently be far more expedient (this would also give the possibility of studying the electronic part of the wave functions). At the present time this is scarcely practical in view of the insufficient quantity of experimental data and the insufficiently high accuracy of the experiment.

Transition to the formulas for the intensities is carried out by arranging the quadratic expressions for the components of the tensor α according to general formulas.[1,2,6]

THE EXPERIMENTAL DATA. COMPARISON OF THEORY WITH EXPERIMENT

For the comparison of theory and experiment we carried out experimental investigations of the intensities of two Raman lines of liquid benzene, due to the valence vibration of the ring ($\omega_{vib.} = 992$ cm^{-1}) and to the valence vibration of the CH bonds ($\omega_{vib.} = 3062$ cm^{-1}), in their dependence on the frequency of the incident light ω_0, and also investigations of one line of p-nitrodimethyl aniline in solution concerning its dependence on the solvent (methyl alcohol ($\omega_{vib.} = 1319$ cm^{-1}) and benzene ($\omega_{vib.} = 1327$ cm^{-1})) and on ω_0. The measurements were carried out photoelectrically in the benzene case and photographically for the p-nitrodimethyl aniline. The method of the measurements has been described in detail elsewhere.[5,9] The excitation was provided by the lines $\lambda_c^0 = 4358$, $\lambda_g^0 = 4047$, $\lambda_f^0 = 3650$, and $\lambda_e^0 = 3131$ A in the benzene case and by the lines $\lambda_c^0 = 5461$ A, λ_g^0, λ_f^0, and λ_e^0 in the p-nitrodimethyl aniline case. The results of the measurements are presented in Table 1 which also contains data obtained from theoretical calculations derived in the following manner.

Table 1

Benzene ($\omega_{vib.} = 992$ cm^{-1})				Benzene ($\omega_{vib.} = 3062$ cm^{-1})			p-Nitrodimethyl aniline		
Quantity	Experiment	Calculated from formula (18)	Calculated according to Placzek	Experiment	Calculated from formula (18)	Calculated according to Placzek	Quantity	In methyl alcohol	In benzene
$\frac{I_2}{I_1}$	1.5	1.5	2.0	1.4	1.3	1.8	$\frac{I_f}{I_c}$	74	83
$\frac{I_f}{I_c}$	3.2	3.2	6.5	2.1	2.0	4.2	$\frac{I_g}{I_c}$	182	481
$\frac{I_e}{I_c}$	10.3	18.3	70	4.1	4.7	19	$\frac{I_e}{I_c}$	780	4207

The analysis of the frequency dependence of the intensities of the benzene lines 992 and 3062 cm^{-1} allows us to surmise that, for the 992 cm^{-1} line, the electronic absorption band located at $\omega_{j0} = 4 \times 10^4$ cm^{-1} appears to be far the most important, and for the 3062 cm^{-1} line the band at 5×10^4 cm^{-1} (cf. also reference 8). In addition, we assumed that in the wavelength interval examined the term proportional to $(\partial\omega'_{j0}/\partial Q)_{Q=Q_0}$ is dominant in (17). Then for the intensity it is possible to obtain the following expression

$$I = \left(\frac{\omega}{\omega_0}\right)^4 a_j \left[\frac{\omega_{j0}^2 + \omega_0^2}{(\omega_{j0}^2 - \omega_0^2)^2}\right]^2, \qquad (18)$$

in which for the lines 992 and 3062 cm^{-1} ω'_{j0} is taken equal to 4×10^4 and 5×10^4 respectively (we neglect the influence of the other bands). We also note that in (18) a_j does not depend on ω_0 and has a constant magnitude for a given scattering angle (in our measurements this is $\pi/2$). The positions of the benzene absorption bands are taken from reference 10. Using expression (18) it is possible to calculate only the magnitude of the ratio of intensities, since it contains an unknown parameter a_j. For comparison we also made calculations taking account of both terms in (17). (In this we assumed for simplicity that the nondiagonal elements of the tensor α differing from zero have identical values.) Then, in addition to a_j appears still another parameter, the value of which was determined by the magnitude of the ratio I_b/I_a, and following this I_f/I_c and I_g/I_c were calculated. In the results in place of 3.2 and 18.3 (the case of $\omega_{vib.} = 992$ cm^{-1}) 3.0 and 16 are obtained, and in place of 2.0 and 4.7 ($\omega_{vib.} = 3062$ cm^{-1}) 2.3 and 6.3. Hence, in this case the assumption regarding the role of the second item in (17) is confirmed.

Table 1 also contains results of calculations made on the basis of Placzek's theory. With analogous assumptions this formula differs from (18) in that the ratio $(\omega/\omega_0)^2$ is replaced by ω^4. Therefore, the values of I/I_a, calculated according to Placzek, differ from the value found from (18) approximately by the factor $(\omega/\omega_a)^4$. As is seen from Table 1 the results of the calculations, carried out with formula (18), agree far better with experiment than the Placzek calculations. This testifies to the merits of the formulas presented in the present work, while simultaneously verifying the assumptions made in writing (18).

In some studies experimental data are presented which are in more or less satisfactory agreement with the formula $I = \text{const.} \times \omega^4$, resulting from Placzek's formulas for a sufficient distance from an absorption band. However, it is frequently proven that the degree of removal, which is actually practical, is insufficient to neglect the dependence on ω_0 of the denominators in formulas analogous to (17). Data, characterizing a typical case of this kind, occur in the left half of Table 2: the nearest significant absorption band is located at a frequency of 4×10^4 cm^{-1}, the wavelengths of the incident light are λ_c^0, λ_g^0, λ_f^0, and λ_e^0, $\omega_{vib.} = 10^3$ cm^{-1}. (A′ and A″ correspond to the squares of the first and second items in the figured brackets in (17), and in the sum there is retained only one term, corresponding to the nearest significant band.) From the Table it is seen that in such cases the frequency dependence which actually occurs (due to the dependence on ω_0 of the quantities A′ and A″) can by chance approximately correspond to the law $I = \text{const.} \times \omega^4$ (particularly if it is assumed that in (17) the second term dominates). We see such a possibility actually occurring in reference 8 (data for CCl_4). Particularly convincing would be an experiment, set up under other conditions (e.g., the conditions corresponding to the right-hand side of Table 2: the most significant absorption band is assumed to be located at a frequency $\omega_{j0} = 4 \times 10^4$ cm^{-1}, the scattered light contains the frequencies $\omega_1 = 10^4$, $\omega_2 = 1.5 \times 10^4$, and $\omega_3 = 2 \times 10^4$ cm^{-1}). In this case the dependencies resulting from (17) and from the law $I = \text{const.} \times \omega^4$ would be, as seen from Table 2, substantially different. Experiments performed under similar conditions are unknown to the authors.

In conclusion, we will examine the results of the investigation of the Raman scattering of p-nitrodimethyl aniline dissolved in methyl alcohol and benzene (Table 1). Attempts to make a comparison of theory and experiment, similar to the benzene case, are not successful since, first, the condition of adequate removal of ω_0 from an absorption band is violated (there is a band near 3850 A), and secondly, on the short wavelength side of the 3850 A band there is a far more intense band, whose parameters are inadequately known. This band undoubtedly strongly influences the intensity in the examined frequency interval, testified by the continued growth of the intensity beyond the maximum of the first band (see Table 1). Data on the influence of solvent on the scattering intensity is of considerable interest, independent of the question of

Table 2

$\omega'_j = 4 \times 10^4$ cm^{-1}				$\omega'_{j0} = 4 \times 10^4$ cm^{-1}, $\omega_1 = 10^4$ cm^{-1}		
Quantity	ω_j^0	ω_a^0	ω_f^0	Quantity	$\omega_2 = 1.5 \times 10^4$ cm^{-1}	$\omega_3 = 2 \times 10^4$ cm^{-1}
$\frac{A'}{A_a}$	1.4	1.8	2.2	$\frac{A'}{A_1}$	1.2	1.8
$\frac{A''}{A_a}$	2.3	3.8	7.3	$\frac{A''}{A_1}$	1.8	3.4
$\left(\frac{\omega}{\omega_a}\right)^4$	2.8	3.5	5.4	$\left(\frac{\omega}{\omega_1}\right)^4$	5.1	16

the relation between I and ω. From Table 1 it follows that the growth of the intensity on increasing ω is faster in the case of solvents whose molecules have a smaller dipole moment. A possible qualitative explanation of this fact is presented below. The attractive forces between molecules (depending on the magnitude of the dipole moments) lead to an increase of the "openness" of the molecules. Then the steepness of the potential curves decreases and the relative role of the second term in (17), containing $[\partial\omega_{ik}^2(Q)/\partial Q]_{Q=Q_0}$, in the given case decreases. Therefore, for greater interaction of the molecules the growth of I is weaker in its dependence on ω. Of course, the authors do not insist on the generality of this fact since the experimental material for this is insufficient. Further investigations in this direction are necessary.

The literature data of Shorygin[11] devoted to this question should be noted. However, he used only one common exciting line [located further from an absorption band than the lines λ_k^0 and λ_i^0 in our case] for the different solvents. Therefore, the indicated data are inadequate for a unique conclusion.

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FORCE CONSTANTS AND INTERACTION COEFFICIENTS OF PYRAMIDAL HYDRIDES

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On the basis of new values of the zero-order frequencies, the force fields of pyramidal hydrides of the type RH_3 (R = N, P, As, Sb) have been studied.

In the present work, a study of the force fields of pyramidal hydrides of the type RH_3 has been completed, a potential function of the following form being used:

$$2V = K_r \sum q_i^2 + h \sum q_i q_j + 2ar \sum q_i \alpha_{ij} + br \sum q_i \alpha_{jk} + \frac{1}{2} K_\alpha r^2 \sum \alpha_{ij}^2 + l r^2 \sum \alpha_{ij} \alpha_{jk}, \quad (i, j, k = 1, 2, 3;\ i \neq j \neq k), \quad (1)$$

where q_i are the changes in the lengths of the R-H valence bonds, the equilibrium value of which equals r; α_{ij} are the changes in the H-R-H angles; K_q, K_α, a, b, h, and l are the desired unreduced force coefficients in the symbols adopted in reference 1.

The force coefficients of the compounds here considered have been calculated by many investigators. Some of them have described the force field by a potential function of another form (see, for example, references 2-6). The latest works in which a potential function of the form (1) was employed are cited in references 7 and 8. For evaluation of the force constants, values of the zero-order frequencies (ω_i) taken from references 2-4 and 8 were used. The zero-order frequencies, as was shown earlier,[9] must satisfy the order rule. However, this is not so in the case of the frequency ω_2 of the ND_3 molecule, as determined in reference 2, and the frequency ω_3 of the AsD_3 molecule.[3]

More exact values of the quantities ω_i for the class of compounds under consideration were recently computed.[10] On the basis of these data, we have carried out new evaluations of the coefficients of expression (1), while accomplishing for the first time the calculation of the corresponding influence coefficients.

The set of equations used in the present work for the determination of the force constants has been previously presented by us (see formulas (3) of reference 9). The vibrational and structural parameters necessary for the calculations were taken from references 10 and 11. The solution of the designated set of equations was first carried out in a general form. In doing so, the fourth equation was discarded, since it must be identical with the third when zero-order frequencies are used. The following expressions were obtained for the reduced force constants (symmetry A_1):

$$v_1 = K_r + 2h = a_0 (a_1' S - a_1 S' + 2R_1), \quad (2)$$

where

$$a_0 = \frac{a}{3m\,(m_1 - m)},\quad a_1 = m_1 [(M + 6m) - 2\,(2M + 3m)\cos\varphi]; \quad (2a)$$

$$v_2 = b + 2s = b_0 (b_1' S - b_1 S' - b_2 R_1), \quad (3)$$

where

$$b_0 = a_0 \sin\varphi,\quad b_1 = m_1\,(2M + 3m),\quad b_2 = \frac{1 - 4\cos\varphi}{2\,(1 - \cos\varphi)\,(1 + 2\cos\varphi)}; \quad (3a)$$

$$v_3 = K_\alpha + 2l = c_0 (c_1 S' - c_1' S - 2R_1), \quad (4)$$

where

$$c_0 = \frac{a_0\,(1 + \cos\varphi)}{2\,(1 + 2\cos\varphi)},\quad c_1 = m_1 [(M - 3m) - 2\,(2M + 3m)\cos\varphi]; \quad (4a)$$

$$R_1^2 = d_0 (d_1 S' + d_2 S S' + d_1' S'^2 + d_3 p), \quad (4b)$$

where

$$d_0 = 2M\,(1 - \cos\varphi)\,(1 + 2\cos\varphi),\quad d_1 = -m^2\,(M + 3m_1),$$

$$d_2 = m m_1\,(2M + 3m + 3m_1),\quad d_3 = -9\,\frac{m^2\,(m_1 - m)^2}{M + 3m}. \quad (4c)$$

For the symmetry E, analogous calculations lead to the following expressions:

$$v_4 = K_r - h = e_0 (e_1 S - e_1' S' + e_2 R_2), \quad (5)$$

where

$$e_0 = \frac{a_0}{1 - \cos\varphi},\quad e_1 = m [3m_1 (1 - \cos\varphi)^2 - M\,(1 + 2\cos\varphi)\,(2 + \cos\varphi)],$$

$$e_2 = \frac{2M}{e}\,(2 + \cos\varphi),\quad e = M\,(2 + \cos\varphi) + 3m\,(1 - \cos\varphi); \quad (5a)$$

$$v_5 = b - a = f_0 (f_1 S' - f_1' S - f_2 R_2), \quad (6)$$

where

$$f_0 = e_0 \sin\varphi,\quad f_1 = m_1 [3m\,(1 - \cos\varphi) + 2M\,(2 + \cos\varphi)],$$

$$f_2 = \frac{M\,(1 + 2\cos\varphi)}{e\,(1 - \cos\varphi)}; \quad (6a)$$

$$v_6 = K_\alpha - l = g_0 (g_1 S - g_1' S' - g_2 R_2), \quad (7)$$

where

$$g_0 = e_0\,(1 + \cos\varphi),$$

$$g_1 = m [3m_1 (1 - \cos\varphi) + M\,(1 + 2\cos\varphi)],\quad g_2 = \frac{2M}{e}; \quad (7a)$$

$$R_2^2 = h_0 [-e\,(h_1 S^2 - h_2 S S' + h_1' S'^2) - h_3 p], \quad (7b)$$

where

$$h_0 = \frac{1 - \cos\varphi}{M}\,e,\quad h_1 = m^2 e',\quad h_2 = m m_1\,(e + e'),$$

$$h_3 = 9m^2\,(m_1 - m)^2\,(1 - \cos\varphi)^2. \quad (7c)$$

Here M, m, and m_1 are the masses of the atoms R, H, and D respectively; φ is the valence angle; $S = \omega_k^2 + \omega_l^2$, $p = \omega_k^2 \omega_l^2$ (RH_3 molecule), $S' = \omega_k'^2 + \omega_l'^2$ (RD_3), where k = 1, l = 2 for symmetry A_1, and k = 3, l = 4 for symmetry E. The quantities represented by lower-case Latin letters from a_1 to h_1 with primes are obtained from the corresponding quantities without primes by means of the replacement of m by m_1 and m_1 by m. The conversion factor α has been introduced into the formulas; when $\alpha = 1$, the force constants are expressed in cm^{-2}; when $\alpha = 4\pi^2 c^2 m = 0.059371$, they are in dynes/cm. The signs of the radicals R_1 and R_2 have been chosen on the basis of numerical analysis and the physical considerations usual in such cases.

The formulas obtained make it possible to evaluate the force coefficients of molecules of analogous structure without preliminary setting-up of the secular equations.

In carrying out the evaluations of the numerical co-

Table 1. Values of the Reduced Force Constants (in mdynes/A) and of their Absolute Errors (in 10^{-3} mdynes/A)

Molecule	Symmetry	i	Reduced force constants v_i		$\Delta v_i(\omega_0)$	$\Delta v_i(\omega_1)$	$\Delta v_i(\omega_k')$	$\Delta v_i(\omega_l')$	$\Delta v_i(m)$	$\Delta v_i(m_1)$	$\Delta v_i(M)$	$\Delta v_i(\varphi)$	$\Sigma \Delta v_i$
			Path I	Path II									
NH_3	A_1	1	6.908	6.904	41	7.5	32	11	1.5	0.40	0.00076	0.28	94
		2	0.0144	0.0164	140	48	190	65	4.9	2.4	0.013	46	500
		3	0.5184	0.5198	1.2	4.4	1.4	0.50	0.0055	0.018	0.00065	14	22
	E	4	7.140	7.125	41	9.5	30	14	1.8	0.44	0.00068	1.6	98
		5	−0.0948	−0.0721	100	47	140	60	4.0	1.9	0.021	24	380
		6	0.6428	0.6448	0.60	4.1	1.0	0.44	0.057	0.0014	0.00028	5.0	11
PH_3	A_1	1	3.403	3.393	27	6.0	18	8.0	0.69	0.17	0.000068	0.5	60
		2	0.0251	0.0287	120	55	180	75	3.5	1.7	0.0035	16	450
		3	0.3068	0.3146	0.90	3.6	1.8	0.80	0.055	0.012	0.000037	4.6	12
	E	4	3.427	3.424	28	6.0	18	8.0	0.65	0.15	0.000062	0.14	59
		5	−0.0217	−0.0252	210	95	290	140	6.0	2.9	0.0057	17	760
		6	0.3698	0.3720	1.2	3.8	1.8	0.75	0.080	0.026	0.000030	1.8	9.4
AsH_3	A_1	1	2.828	2.836	18	2.2	7.0	3.1	0.41	0.064	0.000021	0.60	31
		2	0.0277	0.0258	260	120	360	160	6.6	3.3	0.0013	13	910
		3	0.2780	0.2741	4.2	4.8	6.0	2.6	0.13	0.053	0.000011	2.3	20
	E	4	2.892	2.858	9.0	1.8	5.5	2.5	0.18	0.051	0.000068	0.44	21
		5	−0.0359	−0.0345	470	220	660	300	12	6.1	0.0020	14	1700
		6	0.2815	0.2985	8.5	7.0	12	5.5	0.25	0.11	0.000033	1.2	34
SbH_3	A_1	1	2.292	2.283	6.0	2.4	8.0	3.2	0.099	0.063	0.0023	0.45	20
		2	0.0230	0.0224	380	160	520	220	8.5	4.2	0.06	8.5	1300
		3	0.1879	0.1921	9.0	6.0	12	5.0	0.22	0.10	0.0012	1.6	34
	E	4	2.217	2.293	29	14	55	24	0.70	0.48	0.0017	0.85	120
		5	−0.0277	−0.0394	650	240	950	400	15	7.7	0.095	11	2300
		6	0.3479	0.2103	26	12	36	16	0.61	0.29	0.0036	0.55	91

efficients, we discovered a marked sensitivity of their values to the choice of the path of calculation; this is illustrated by the data of Table 1, in which are presented the quantities v_i computed according to formulas (2)-(7) (path I) and by direct solution of set (3) of reference 9, averaging the third and fourth equations (path II). The nondiagonal coefficients v_2 and v_5 proved to be particularly sensitive to the choice of the path of calculation. In subsequent computation, the data of the second calculation are used.

Let us now consider the question of the influence of errors in the values of the starting parameters—ω_k, ω_l, ω_k', ω_l', m, m_1, M, and φ—on the accuracy of the determination of the values of v_i. Let t_j be any of these parameters; then the partial error $\Delta v_i(t_j)$ brought about by the presence of the error Δt_j will be expressed, on the basis of a well-known formula of error theory, in the following way:

$$\Delta v_i(t_j) = \left| \frac{\partial v_i}{\partial t_j} \right| \Delta t_j. \qquad (8)$$

i.e., the problem reduces to evaluation of the derivatives $\partial v_i/\partial t_j$. When formulas (2)-(7) are available, the problem is solved by simple differentiation of these formulas (first method). In the case where expressions of this type are not at our disposal, the following procedure may be employed (second method). We shall consider the first three equations of set (3) of reference 9 as complex (implicit) functions of the given parameter t_j

$$f_n[v_i(t_j),\ t_j] = 0,\ (n = 1,\ 2,\ 3). \qquad (9)$$

Differentiating each of the equations with respect to the parameter t_j, we obtain a set of three linear equations of the form

$$\sum_i \frac{\partial f_n}{\partial v_i} \frac{\partial v_i}{\partial t_j} + \frac{\partial f_n}{\partial t_j} = 0,\ (n = 1,\ 2,\ 3). \qquad (10)$$

Solution of the set with respect to $\partial v_i/\partial t_j$ may be carried out by using Gauss's alogarithm (see, for example, reference 12). The second method is very convenient on account of the fact that the sets of equations (10) for various t_j differ only in the sets of free terms, as a result of which the possibilities for standardizing the calculations increase. A check of the evaluation of the derivatives is easily accomplished by using Euler's theorem on homogeneous functions. It should be noted that the numerical values of the quantities $\partial v_i/\partial t_j$ possess a marked sensitivity to the choice of the path of calculation; however, this proves to be insignificant for estimation of the over-all error.

The average errors of the starting parameters, which are necessary for the evaluation of the quantities $\Delta v_i(t_j)$, were taken as equal to the following: $\Delta\omega_k = \Delta\omega_l = \Delta\omega_k' = \Delta\omega_l' = 5\ cm^{-1}$; $\Delta m = \Delta m_1 = \Delta M = 10^{-4}$ atomic weight units (except for the SbH_3 molecule, for which $\Delta M = 10^{-3}$), and $\Delta\varphi = 0.5°$ (0.00875 radians). The results of the calculations (carried out by the second method) of the partial errors in the reduced force constants are presented in Table 1, in which the quantities v_i are expressed in mdynes/A, $\Delta v_i(t_j)$ and $\Sigma \Delta v_i(t_j)$ in 10^{-3} mdynes/A. It can be seen from the table that the sensitivity of the force coefficients to the choice of path of calculation is considerably less than the sensitivity to errors in the starting parameters. It is also easy to note that the accuracy of the determination of the quantities v_i depends principally on the accuracy of the values of the zero-order frequencies and of the valence angles. Stretching frequencies, as a rule, give a greater partial error than deformation frequencies. The coefficients of composite interaction, v_2 and v_5, whose partial errors have a tendency to increase with an increase in mass of the central atom, possess an especially high sensitivity to variation in the starting parameters.

Furthermore, from the values of the reduced force coefficients (v_{ij}) indicated in Table 1, values of the reduced interaction coefficients (u_{ij}) have been calculated on the basis of the relationship

$$VU = E, \qquad (11)$$

where $V = \| v_{ij} \|$ and $U = \| u_{ij} \|$ are the matrices of the force coefficients and the interaction coefficients respectively, and E is the unit matrix. At the same time, the values of the errors Δu_{ij} were evaluated on the basis of the total error values Δv_{i_m} presented in Table 1. The values of the derivatives $\partial u_{ij}/\partial v_{i_m}$ necessary for this purpose may be obtained by differentiating the equality (11)

$$\frac{\partial V}{\partial v_{i_m}} U + V \frac{\partial U}{\partial v_{i_m}} = 0, \qquad (11a)$$

whence

$$\frac{\partial U}{\partial r_{lm}} = -U\frac{\partial V}{\partial r_{lm}}U. \qquad (12)$$

In the case where the matrix V contains no other elements identical in the physical sense with v_{lm}, then

$$\frac{\partial V}{\partial r_{lm}} = E_{lm}, \qquad (12a)$$

where E_{lm} is the matrix in which unity stands at the intersection of the lth row and the mth column and the remaining elements are zero. Comparison of the matrix elements on the left and right sides of the equality (12) gives

$$\frac{\partial u_{ij}}{\partial r_{lm}} = -u_{il}u_{mj}. \qquad (13)$$

But if some elements of the matrix V denote one and the same force coefficient (for example, $v_{lm} = v_{s1}$), then

$$\frac{\partial V}{\partial r_{lm}} = E_{lm} + E_{sl} \qquad (13a)$$

and the derivative sought is expressed as a sum of products composed according to the pattern of (13). The method just described is particularly convenient when one is considering high-order matrices. The values of the unreduced dynamic coefficients and the corresponding errors are presented in Table 2.

Table 2. Values of the Unreduced Force Constants (in mdynes/A), Interaction Coefficients (in A/mdyne), and their Errors (in %)

Dynamic coefficient	NH_3		PH_3		AsH_3		SbH_3	
K_r	7.053	1.4	3.414	1.7	2.850	0.84	2.289	3.8
K_α	0.6034	2.5	0.3528	2.8	0.2904	10	0.2042	35
a	0.0295	980	0.0180	2300	0.0201	4300	0.0206	5800
b	—0.0427	980	—0.00720	9200	—0.0144	9700	—0.0188	11000
h	—0.0737	87	—0.0102	390	—0.00733	220	—0.00347	1900
l	—0.0417	26	—0.0191	37	—0.00813	220	—0.00607	690
K_r'	0.1419	2.3	0.2931	4.5	0.3513	12	0.4379	33
K_α'	1.876	3.6	2.854	5.8	3.453	21	4.917	63
a'	—0.00676	1100	—0.0158	2200	—0.0248	4300	0.0444	5900
b'	0.00695	1100	0.00420	13000	0.0458	11000	0.0376	11000
h'	0.00145	150	0.000907	960	0.000833	3100	0.00038	23000
l'	0.124	36	0.184	71	0.0987	450	0.147	1200

Beyond this, the following dependences were studied and are presented graphically (see references 13 and 14):

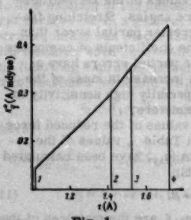

Fig. 1

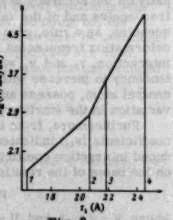

Fig. 2

Fig 1. 1—NH_3; 2—PH_3; 3—AsH_3; 4—SbH_3.
Fig. 2. Symbols the same as in Fig. 1.

(a) between the interaction coefficients for bond stretching K_q^* and the equilibrium distances r = R-H (Fig. 1); (b) between the interaction coefficients for angle deformation K_α^* and the equilibrium distances r_1 = H-H (Fig. 2); (c) between the logarithms of the force constants for bond stretching K_q and for angle deformation K_α (Fig. 3). As can be seen from the figures, all three dependences are sufficiently close to being linear. The greatest deviation from linearity is observed in Fig. 2, but even in this case it does not exceed the possible errors in the determination of the values of the unreduced influence coefficients.

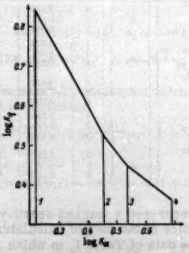

Fig. 3. The dimensions of the quantities K_q and K_α are given in mdynes/A; for the symbols 1-4 see legend to Fig. 1.

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CONDITIONS FOR SPECIFICITY OF INFRARED BAND INTENSITIES IN POLYATOMIC MOLECULES

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The conditions for specificity of the intensities of infrared absorption bands corresponding to the normal vibrations of polyatomic molecules have been theoretically considered. As a quantitative criterion of the specificity of the intensity of a vibration, the coefficient of non-specificity of intensity, γ, has been introduced. The applicability of the conditions formulated for the specificity of the integrated intensities of infrared bands is illustrated by a complete series of examples.

1. Investigation of the vibrational spectra of compounds of various classes has shown that, as a rule, the spectra of molecules possessing identical structural groups have a certain number of frequencies which correspond closely in numerical value and which have received the designation of "characteristic" or "specific." At the same time, it has been made clear that the characteristic vibrations are often distinguished also by a constant intensity. This important property of some characteristic vibrations is widely applied in molecular spectroscopy for the solution of various problems. For example, quantitative spectral analysis for structural groups is based on this phenomenon. Furthermore, in recent years more and more works have appeared in which, on the basis of intensity changes in characteristic lines on going from one class of compounds to another, various conclusions (often unsubstantiated, to be sure) are drawn concerning a change in the polarity and character of the chemical bonds.

In this connection, it is of interest to consider theoretically the conditions for specificity of the intensities of normal vibrations, especially of infrared band intensities, similarly to the way in which Mayants[1] theoretically established the conditions for specificity of vibrations with respect to frequency and form.

2. Let us consider some polyatomic molecules with n vibrational degrees of freedom. Let us pick out some group of n′ internal coordinates of the molecule—coordinates connected with a definite structural element—without change in the parameters corresponding to them in the molecule.

In this case, if the intensity of some normal vibration of the molecule is close to the intensity of one of the normal vibrations of this group of coordinates, we shall designate such a normal vibration as specific with respect to intensity for the given group of coordinates. In the case of exact coincidence of the intensity of some normal vibration of the molecule with one of the normal vibrations of the given group of coordinates, we shall designate such a normal vibration as completely specific with respect to intensity for the given group of coordinates.

The concept of specific intensity which has accumulated in the literature—as a vibrational intensity which accompanies a definite structural group in a series of compounds containing that group—is associated with the stability of the specificity; i.e., with the retention of the specificity of intensity for a given group of coordinates (those which describe that structural element) on going from one compound to another.

As a quantitative criterion of the specificity of the intensity of a molecular vibration for a given group of coordinates, we introduce the coefficient of nonspecificity of intensity, γ, determined by the expression

$$\gamma = \frac{I_l - I_{l'}}{I_{l'}}, \tag{1}$$

where I_l is the intensity of the l-th normal vibration of the molecule and $I_{l'}$ the intensity of the l′-th normal vibration of this group of coordinates, considered in isolation. The ambiguity associated with the presence of n′ different γ's (if the group consists of n′ coordinates) may be removed by choosing that γ which is least in absolute magnitude. In the case of complete specificity of intensity, $\gamma = 0$.

3. In order to clarify the conditions necessary for specificity of the intensity of the infrared band corresponding to the l-th normal vibration of the molecule, let us write down formula (1) in expanded form.

The integrated intensity of an infrared band is proportional to the square of the derivative of the molecular dipole moment p with respect to the normal coordinate Q_l [2, 3]

$$I_l = \frac{\pi N}{3c}\left[\frac{\partial \mathbf{p}}{\partial Q_l}\right]^2 \sim \left[\frac{\partial \mathbf{p}}{\partial Q_l}\right]^2. \tag{2}$$

Taking into account the connection between the normal coordinate Q_l of the molecule and the symmetry or internal coordinates S_k,

$$\begin{aligned} S'_k &= \sum_{l=1}^{n} L'_{kl} Q_l \quad (k = 1, 2, \ldots n'); \\ S''_k &= \sum_{l=1}^{n} L''_{kl} Q_l \quad (k = n'+1, \ldots, n), \end{aligned} \tag{3}$$

we obtain

$$\begin{aligned} I_l \sim \left[\sum_{k=1}^{n} \frac{\partial \mathbf{p}}{\partial S_k}\frac{\partial S_k}{\partial Q_l}\right]^2 &= \left[\sum_{k=1}^{n'} \frac{\partial \mathbf{p}}{\partial S'_k} L'_{kl} + \sum_{k=n'+1}^{n} \frac{\partial \mathbf{p}}{\partial S''_k} L''_{kl}\right]^2 \\ &= \left\{\left[\sum_{k=1}^{n'} \frac{\partial \mathbf{p}}{\partial S'_k} L'_{kl}\right]^2 + 2\left[\sum_{k=1}^{n'} \frac{\partial \mathbf{p}}{\partial S'_k} L'_{kl}\right] \right. \\ &\left. \times \left[\sum_{k=n'+1}^{n} \frac{\partial \mathbf{p}}{\partial S''_k} L''_{kl}\right] + \left[\sum_{k=n'+1}^{n} \frac{\partial \mathbf{p}}{\partial S''_k} L''_{kl}\right]^2\right\}. \end{aligned} \tag{3a}$$

The molecular dipole moment p may be represented in the form of a sum of the dipole moments of the given structural element p′ and of the remaining part of the molecule p″.

$$\mathbf{p} = \mathbf{p}' + \mathbf{p}''. \tag{4}$$

Taking this into account, we have

$$I_l \sim \left\{\left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k} L'_{kl} + \sum_{k=1}^{n''} \frac{\partial p''}{\partial S''_k} L''_{kl}\right]^2 + 2\left[\sum_{k=1}^{n'} \frac{\partial p}{\partial S'_k} L'_{kl}\right]\left[\sum_{k=n'+1}^{n} \frac{\partial p}{\partial S''_k} L''_{kl}\right] + \left[\sum_{k=n'+1}^{n} \frac{\partial p}{\partial S''_k} L''_{kl}\right]^2\right\}. \quad (5)$$

Analogously, for the given structural element and the group of coordinates n′ corresponding to it, we obtain for the intensity of the l′-th normal vibration

$$I_{l'} \sim \left[\frac{\partial p'}{\partial Q_{l'}}\right]^2 = \left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k} \frac{\partial S'_k}{\partial Q_{l'}}\right]^2 = \left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k} L_{kl'}\right]^2. \quad (6)$$

Substituting (5) and (6) in (1), we obtain

$$\gamma = \frac{\left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k}(L'_{kl} - L_{kl'}) + \sum_{k=1}^{n''} \frac{\partial p''}{\partial S''_k} L''_{kl}\right] \cdot \left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k}(L'_{kl} + L_{kl'}) + \sum_{k=1}^{n''} \frac{\partial p''}{\partial S''_k} L''_{kl}\right] + 2\left[\sum_{k=1}^{n'} \frac{\partial p}{\partial S'_k} L'_{kl}\right] \cdot \left[\sum_{k=n'+1}^{n} \frac{\partial p}{\partial S''_k} L''_{kl}\right] + \left[\sum_{k=n'+1}^{n} \frac{\partial p}{\partial S''_k} L''_{kl}\right]^2}{\left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k} L_{kl'}\right]^2} + \frac{}{\left[\sum_{k=1}^{n'} \frac{\partial p'}{\partial S'_k} L_{kl'}\right]^2}. \quad (7)$$

As follows from (7), in order for the coefficient of nonspecificity of intensity to have a minimum value and consequently for the intensity to be specific, the following conditions must be satisfied:

(a) The l-th normal vibration of the molecule must be specific for the given group of coordinates; i.e., it must be close in frequency and form to the l′-th normal vibration of the given group of coordinates

$$L'_{kl} \approx L_{kl'} (k = 1, 2, \ldots n'); \; L''_{kl} \approx 0 \; (k = n'+1, \ldots n). \quad (8)$$

The requirement for specificity of the frequency follows from the normalization conditions for the coefficients $L_{kl} = N_l R_{kl}$, since the normalizing factor

$$N_l^2 = \frac{\nu_l^2}{\sum_{ij} K_{ij} R_{il} R_{jl}} \quad (8a)$$

depends on the frequency (here K_{ij} are the force constants and R_{il} the unnormalized form coefficients).

(b) $$\left|\frac{\partial p''}{\partial S''_k}\right| \ll \left|\frac{\partial p'}{\partial S'_k}\right|, \quad (9)$$

i.e., the derivatives of the dipole moment of the remaining part of the molecule with respect to the coordinates of the given structural group must be small in comparison with the derivatives of the dipole moment of the given structural group with respect to the coordinates of that group.

(c) $$\left|\frac{\partial p}{\partial S''_k}\right| = \left|\frac{\partial p'}{\partial S''_k} + \frac{\partial p''}{\partial S''_k}\right| \quad (9a)$$

must not be very large, and specifically such that

$$\left|\frac{\partial p}{\partial S''_k} L''_{kl}\right| \approx 0. \quad (9b)$$

Finally, in order for the specificity of intensity to be stable—i.e., for retention of specificity in some series of compounds containing the given structural group—still a fourth condition must be fulfilled. The derivatives of the dipole moment of the given structural group with respect to the coordinates of that group, $\partial p'/\partial S'_k$, must not change significantly on going from one molecule to another; i.e., the interaction of the electron clouds of the two parts of the molecule must be so small that the electro-optical parameters of the given structural group remain almost constant on attachment of any substituent to the molecule.

The fulfillment of the first condition may be tested by Mayants' procedure.[1] As for the fulfillment of the other three conditions, they can only be tested through evaluation of $\partial p/\partial S_k$ for several molecules containing the identical structural group, using the observed intensity values for this purpose. This is at the present time the only sufficiently accurate method, in consequence of the practical impossibility of a strict quantum-mechanical calculation (to be sure, in some cases approximate qualitative estimates are possible).

The conditions for specificity of intensity which we have considered refer to isolated molecules; i.e., to the substance in the gaseous phase. If we go over to the liquid or to solutions, then, as a result of intermolecular interaction, the electro-optical parameters of the molecule may change, especially in polar solvents, and consequently the intensities will change even when the specificity of the frequency and form of the vibration is retained.

4. We present some examples illustrating the conditions we have formulated for the specificity of the integrated intensity of infrared bands.

(a) First of all, let us consider the intensities of some vibrations of the deuterioethylenes.[4, 5] In this case, a change of intensity on going from ethylene to the various deuterioethylenes takes place only in consequence of a change in frequency or form of the vibration, inasmuch as the electro-optical parameters remain unchanged. For example, the vibration ν_9 (3105 cm^{-1}) of ethylene appears specific in frequency and form for the group of coordinates which includes changes in the lengths of all four C—H bonds. On going over to groups of coordinates containing changes in the lengths of three C—H bonds (q_{2a}, q_{2b}, q_4) and two C—H bonds (q_{2a}, q_4), the specificity of frequency is not disturbed for either group, but the specificity of form is. Thus the first condition for specificity of intensity is not fulfilled for these two groups. Therefore, the transition in the molecules C_2H_3D and asym-$C_2H_2D_2$, in the spectra of which the frequency ν_9 is almost unchanged (C_2H_3D 3103, asym-$C_2H_2D_2$ 3095 cm^{-1}), is accompanied by a sharp change in the intensity of this band as a result of the change in the form of the vibration:

$A_9(C_2H_4) = 112.4$, $A_9(C_2H_3D) = 82.2$ and

$A_9(\text{asym-}C_2H_2D_2) = 58.7$ cm^{-1}/cm-atm.

(b) Let us next consider some vibrations of the methyl halides CH_3Z.[6] The valence vibrations $\nu_1^{A_1}$ (3062) and ν_5^E (3209 cm^{-1})* of the CH_3Cl molecule are specific in frequency and form for the group of coordinates which includes changes in the lengths of all three C—H bonds. On going over to the molecules CH_3Br and CH_3I, the frequency and form of these vibrations are almost unchanged (CH_3Br 3061, 3213; CH_3I 3060, 3229 cm^{-1}), but the integrated intensities of the infrared bands diminish markedly in this series:

$CH_3Cl - I_1 = 98.9$, $I_4 = 22.7$;

$CH_3Br - I_1 = 84.7$, $I_4 = 10.7$;

$CH_3I - I_1 = 58$, $I_4 = 5.1$ (cm^{-1}/cm-atm).

This is explained by the violation of the second, third,

*The frequencies of infinitely small vibrations are given.

and fourth conditions for specificity of intensity for the vibration ν_1 and the fourth condition for the vibration ν_4; namely

$$\frac{\partial \mu_{CZ}}{\partial q_1} > \frac{\partial \mu_{CH}^{(1)}}{\partial q_1} \qquad (9c)$$

(while according to the second condition the reverse relationship is necessary), $\partial p/\partial q_{CZ}$ is very large and, finally, $\partial \mu_{CH}^{(1)}/\partial q_1$ diminishes in the given series of methyl halides.

In contrast to this, the intensity of the deformation vibration ν_5^+ changes relatively little in the methyl halide series: $CH_3Cl - I_5 = 28.6$; $CH_3Br - I_5 = 27.8$; $CH_3I - I_5 = 24.7$ (cm^{-1}/cm-atm). In the latter case, all the conditions for specificity are sufficiently well fulfilled. First, this vibration is specific in frequency and form for the group of coordinates including changes in all the angles ($CH_3Cl - \nu_5 = 1520$; $CH_3Br - 1506$; $CH_3I - 1504$ cm^{-1}); second, the electro-optical parameters μ_{CH} and $\partial \mu_{CH}/\partial \varphi$ change insignificantly in the methyl halide series.

(c) We have previously shown[7, 8] that the vibrations $\nu(\rho_{CH_2}) = 909$ cm^{-1} and $\nu(\chi_{CH_2}^{CHC}) = 992$ cm^{-1} in alkenes of the type $RCH{=}CH_2$ are specific in frequency and form for the group of nonplanar coordinates associated with the structural group $CHC{=}CH_2$. One may also expect that the electro-optical parameters of the $CH{=}CH_2$ group which are responsible for the intensity of these vibrations, namely, the dipole moments of the =C—H bonds (μ_{CH}), change relatively little on replacement of one of the hydrogen atoms in ethylene by the CH_3 group (the fact that the force constants of the nonplanar vibrations of this group remain practically unchanged under such a substitution[7] speaks especially in favor of this) and remain almost constant on going from propylene, $CH_3CH{=}CH_2$, to subsequent terms of the $RCH{=}CH_2$ series (in consequence of the remoteness from the $CH{=}CH_2$ group of the atoms where the substitution takes place).

Furthermore, the third condition for the specificity of intensity is also fulfilled in this case, since, as we have shown,[8] μ_{CH} and $\partial \mu_{CH}^{(1)}/\partial q_1$ in the CH_3 group are relatively small. Thus, inasmuch as the conditions for specificity are fulfilled, the integrated intensities of the infrared bands of these two vibrations must be specific to a high degree. In particular, the intensities of these bands must be fairly high by analogy with the high intensity of the corresponding vibrations of monodeuteroethylene $CHD{=}CH_2$: $\nu_7(\rho_{CH}) = 943$ cm^{-1}, $I_7 = 143.2$ and $\nu_4(\chi_{CH_2}^{CHD}) = 1001$ cm^{-1}, $I_4 = 50.7$ (cm^{-1}/cm-atm), while there must be about the same ratio between them. Experiment[10, 11] completely confirms this conclusion—both the bands under consideration are very intense and have a constant integrated intensity in the $RCH{=}CH_2$ series, which enables us to determine the structural group $CH{=}CH_2$ quantitatively in the most varied products. In this connection it is interesting to note that, in correspondence with Iogansen's experimental data,[10] the integrated intensity of the 909 cm^{-1} band is two and a fraction times as large as the integrated intensity of the 992 cm^{-1} band (data for liquids), just as the theory predicts.

Analogous considerations may also be applied to the vibration $\nu(\rho_{CH_2}) = 890$ cm^{-1} in alkenes of the type $R'RC{=}CH_2$, which is specific in frequency and form for the group of nonplanar coordinates associated with the structural group $\diagup\!\!\diagdown C{=}CH_2$.[9, 12] The conditions for specificity of intensities are fulfilled for this vibration also, and therefore the integrated intensity of the 890 cm^{-1} infrared band must be specific. In particular, the value of the intensity of this band must be considerable, by analogy with the high value of the intensity of the corresponding vibration of the asym-$C_2H_2D_2$ molecule, $\nu_8(\rho_{CH_2}) = 943$ cm^{-1} ($I_8 = 145$ cm^{-1}/cm-atm; i.e., somewhat larger than $I_7(CHD{-}CH_2)$). Experiment[10] confirms this conclusion: the integrated intensity of the infrared band in question is constant in the $R(CH_3)C{=}CH_2$ series, the intensity of the 890 cm^{-1} band slightly exceeding, according to Iogansen's data,[10] that of the 909 cm^{-1} $RCH{=}CH_2$ band.

(d) Let us consider, finally, some characteristic infrared bands of the normal paraffins. It has repeatedly been shown[1, 2] that a number of vibrations of the CH_3 group (namely, the antisymmetric valence vibration $\nu(q_{CH_3}^-) \approx 2960$ cm^{-1} and the symmetric and antisymmetric deformation vibrations $\nu(\alpha_{CH_3}^+) \approx 1380$ cm^{-1} and $\nu(\alpha_{CH_3}^-) \approx 1450$ cm^{-1}) and of the CH_2 group (the antisymmetric valence vibration $\nu(q_{CH_2}^-) = 2926$ cm^{-1} and the deformation vibration $\nu(\alpha_{CH_2}) = 1463$ cm^{-1}) are specific in frequency and form relative to the group of internal coordinates of CH_2 and CH_3. Furthermore, our calculation of the intensities of the infrared bands and electro-optical parameters of methane and ethane has shown[9] that the replacement of a hydrogen atom in methane by the CH_3 group does not show up very strongly in the electro-optical parameters μ and $\partial \mu/\partial q$ of the CH_3 group (they change by roughly 10-20%). Hence one may draw the conclusion that the replacement of one of the hydrogen atoms in ethane $CH_3{-}CH_3$ by a radical R exerts even less influence on the electro-optical parameters of the CH_3 end group. Consequently, on going from one member of the series of normal paraffins to another, the electro-optical parameters of the CH_3 group will be practically constant. Analogous considerations relative to the constancy of the electro-optical parameters during an increase in the carbon chain may also be applied to the CH_2 groups; however, the electro-optical parameters of the $\diagup\!\!\diagdown CH_2$ group must differ from the corresponding parameters of the C—CH_2 group, since if μ and $\partial \mu/\partial q$ change somewhat on going from CH_4 to $CH_3{-}CH_3$, they must also change on the subsequent replacement of hydrogen in the C—CH_2H group by the CH_3 group. Thus the conditions for specificity of intensity are fulfilled for the vibrations cited above, and consequently the integrated intensities of the infrared bands of these vibrations must be specific. This conclusion is fully confirmed by experiment—many authors[10, 11, 13] have experimentally established the constancy of the integrated intensity of the bands cited above, and these data are widely used in quantitative structural-group analysis.

In conclusion, it should be noted that analogous conditions for the specificity of intensity hold true for Raman spectra also. Here the first condition is retained, but in the second, third, and fourth conditions the components of the polarizability tensor of the given structural element and of the remaining part of the molecule must figure in place of the dipole moments. Numerous examples may be brought forward in confirmation of the applicability of these conditions.[14]

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OPTICAL INVESTIGATION OF THE MOLECULAR STRUCTURE OF CYANAMIDE AND ITS DERIVATIVES

III. Infrared and Ultraviolet Spectra and Molecular Structure of the Products of the Interaction of Cyanamide with Ketones (N-Cyanoketimines)

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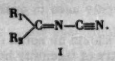
Infrared and ultraviolet spectra have been obtained for the products of the interaction of cyanamide with acetone, methyl ethyl ketone, cyclohexanone, and cyclopentanone. It has been shown that these products represent N-cyanoketimines. It has been established that, in the infrared spectra of the N-cyanoketimine grouping, two frequencies, aside from the band of the C=N bond, are characteristic: $\nu_1 \approx 1650$ cm^{-1} and $\nu_2 \approx 1540$ cm^{-1}; these may be used for the identification of the group. The influence of ring strain on the ultraviolet spectra of N-cyanoketimines has been noted. It has been established that the compounds studied are associated in methanol solution.

While studying the chemical properties of cyanamide, Gol'dberg and Golov[1] discovered that cyanamide enters into reaction with ketones. By analogy with the reaction of ketones with hydrazine, semicarbazide, and hydroxylamine, and also on the basis of elementary analysis, the formula of an N-cyanoketimine



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may be ascribed to the water-insoluble product of this reaction.

The spectroscopic investigation of substances of this type is of considerable interest, since they contain conjugated CN bonds, which have been little studied up to the present time. Interesting conclusions may also be drawn from a comparison of the experimental results with the data previously obtained by us in the study of the dimerization product of cyanamide: dicyandiamide.[2]

In the present work, infrared and ultraviolet absorption spectra have been obtained for the water-insoluble products of the interaction of cyanamide with acetone, methyl ethyl ketone, cyclohexanone, and cyclopentanone.*

*The substances were prepared and purified by V. G. Golov, to whom the authors extend their deep gratitude.

For comparison, the ultraviolet spectra of aqueous solutions of cyanamide and dicyandiamide are also presented.

The infrared spectra of the crystalline substances were studied on samples obtained by pressing a mixture of the substances with NaCl and KBr.[3] For study of the ultraviolet spectra, solutions in methyl alcohol were used.

Absorption spectra in the infrared region were obtained with the help of an IKS-12 single-beam infrared spectrophotometer. Study of the ultraviolet spectra was carried out with the help of an SF-4 spectrophotometer.

In Fig. 1 are presented the infrared spectra of the water-insoluble products of the reaction of cyanamide with ketones. In the spectra of all these substances (with the exception of the reaction product from cyanamide and acetone), there are no absorption bands in the region greater than 3000 cm^{-1} which might be assigned to vibrations of OH or NH groups. This result agrees with the structural formula I presented above. For acetone N-cyanoketimine, there is observed a splitting of the long wavelength band corresponding to vibration of the CH_3 groups, which may serve to indicate the presence of a multiple bond near the methyl group.[4] The presence of a system of conjugated CN bonds in all the compounds investigated leads to a shift of the characteristic frequency of the cyano group in comparison with cyanamide and dimethylcyanamide. We note that such a frequency shift is also observed in the spectrum of dicyandiamide (see Table).

As can be seen from the Table, the frequency values for the vibrations of the CN group in acetone N-cyanoketimine and 2-butanone N-cyanoketimine coincide with the average value of the split vibration frequencies for the CN triple bond in dicyandiamide. The inclusion of the

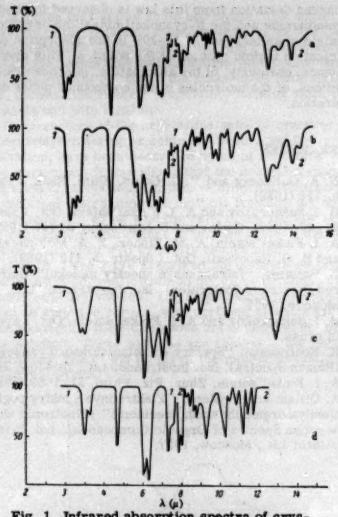
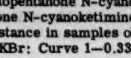


Fig. 1. Infrared absorption spectra of crystalline N-cyanoketimines. a—Acetone N-cyanoketimine; b—2-butanone N-cyanoketimine; c—cyclopentanone N-cyanoketimine; d—cyclohexanone N-cyanoketimine. Content of the test substance in samples obtained by pressing with KBr: Curve 1—0.33%; curve 2—1%.

carbon atom of the cyanamide grouping in a ring is accompanied by a lowering of the frequency of the CN group by ~40 cm^{-1}, and also by a reduction in the intensity of the corresponding band (Fig. 1).

Taking these facts into account and using the set of supplementary conventional symbols,[7] we may depict the structure of the ketone N-cyanoketimines in the following way:



II

The closeness of the values of the vibrational frequencies of the C=N and $\rangle$C=N–C=N groups in the N-cyanoketimines and in dicyandiamide characterizes the closeness of the electronic states of the multiple bonds in these molecules.

Let us now proceed to consideration of the ultraviolet absorption spectra of the N-cyanoketimines. From comparison of the spectra of these compounds (Fig. 2) with the spectrum of cyanamide (Fig. 3a), it can be seen that the absorption coefficient of the cyanoketimines is much larger than that for cyanamide. Hence it follows that the increase in the absorption of N-cyanoketimines in comparison with H_2CN_2, which also contains the C=N group, is connected with the presence of a system of conjugated CN bonds in the N-cyanoketimines. We also note that, for the isolated C=N bond (for example, in acetonitrile), the value $\lambda_{max} < 160$ mμ is given in reference 8 for the wavelength of the maximum of the absorption band. The absorption bands with $\lambda_{max} > 200$ mμ which we have observed correspond, apparently, to a forbidden, unlocated absorption band of acetonitrile which must be situated in the wavelength region greater than 200 mμ.

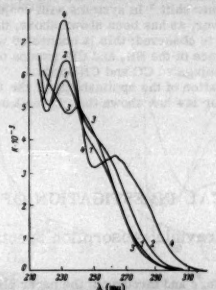


Fig. 2. Ultraviolet absorption spectra of solutions of N-cyanoketimines in methyl alcohol. Curve 1—Acetone N-cyanoketimine; curve 2—2-butanone N-cyanoketimine; curve 3—cyclohexanone N-cyanoketimine; curve 4—cyclopentanone N-cyanoketimine.

Analysis of the ultraviolet spectra of acetone N-cyanoketimine and 2-butanone N-cyanoketimine shows, furthermore, that directly after the absorption band with λ_{max} ~ 232-234 mμ there follows a more intense band whose maximum is situated in the region of wavelengths less than 215 mμ (probably around 190-200 mμ).

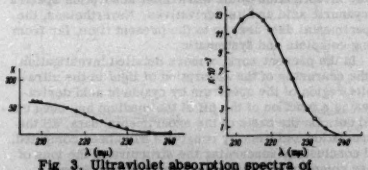


Fig 3. Ultraviolet absorption spectra of aqueous solutions of cyanamide (left) and dicyandiamide (right).

In conclusion, we note that, in the spectra of the cyclic products, a bathochromic band shift is observed as a result of strain in the ring. Thus, in the spectrum

Compound	Vibrational frequencies ν (cm⁻¹)	
	Cyanamide group	Cyanoketimine group
Dicyandiamide[3]	2175 (average)	1840, 1575
Deuteriodicyandiamide[3]	2150	1626, 1538
Acetone N-cyanoketimine	2175	1653, 1530
2-Butanone N-cyanoketimine	2175	1853, 1540
Cyclohexanone N-cyanoketimine	2135	1840, 1580
Cyclopentanone N-cyanoketimine	2135	1840, 1540
Cyanamide[3]	2242	—
Dimethylcyanamide[3]	2233	—

of cyclohexanone N-cyanoketimine the maximum of the long wavelength band is at 240 mμ, and in the spectrum of cyclopentanone N-cyanoketimine this band is still further displaced toward the red part of the spectrum (λ_{max} = 264 mμ), while in the region accessible for measurement there appears an additional short wavelength band with λ_{max} = 232 mμ.

Ring strain also manifests itself in the intensity of the absorption. Thus the absorption coefficient at the maximum (K_{max}) in the aliphatic N-cyanoketimines equals 6000-6500, in cyclohexanone cyanoketimine it is 5100, and in cyclopentanone N-cyanoketimine, in which the ring strain is particularly large, K_{max} falls to 3700. On replacement of the alkyl radicals by NH_2 groups (Fig. 3b), the absorption intensity of the cyanoketimine grouping increases and a shift of the band maxima into the short wavelength region of the spectrum takes place (λ_{max} = 215 mμ).

It is interesting to note that in the case of the so-called K-bands corresponding to absorption by dienic and polyenic structures of the type —(CH=CH)— and —(C≡C)—, replacement of a CH_3 group by NH_2 leads to a bathochromic shift.[8] In systems with conjugated CN bonds, however, as has been shown above, the opposite phenomenon is observed; this is connected with the different influence of the NH_2 and CH_3 groups on the electron density in conjugated CC and CN bonds.

Investigation of the applicability of the Lambert-Bouguer-Beer law has shown that, in methanol solutions, a marked deviation from this law is observed for both dicyandiamide and the N-cyanoketimines; the deviation consists of an increase of 15-20% in the absorption coefficient on tenfold dilution of the solution. This gives evidence, obviously, of the association, in concentrated solutions, of the molecules of the compounds under consideration.

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OPTICAL INVESTIGATION OF THE MOLECULAR STRUCTURE OF s-TRIAZINE DERIVATIVES

VI. Ultraviolet Absorption Spectra of Aqueous Solutions of Cyanuric Acid Derivatives at Various pH*

*Here and throughout the paper pH denotes the negative logarithm of the hydrogen ion activity, paH.

E. N. Boitsov and A. I. Finkel'shtein

Received 28 October 1959

The absorption spectra, in the ultraviolet region, of aqueous solutions of melamine, ammeline, ammelide, cyanuric acid, and trimethoxy-s-triazine have been studied at various pH values from −2.6 to 15. The basicity constants for melamine ($K_{b_3} < 10^{-17}$), ammeline ($K_{b_2} = 3.97 \times 10^{-10}$), and trimethoxy-s-triazine ($K_{b_1} < 1.6 \times 10^{-14}$), and also the dissociation constant of cyanuric acid ($K_{a_3} = 3.16 \times 10^{-14}$), have been determined for the first time. Diagrams of the equilibrium of the acid-base forms of the molecules studied are presented

A considerable number of works[1-3] have been devoted to the investigation of the ultraviolet absorption spectra of cyanuric acid and its derivatives. Nevertheless, the experimental data are, up to the present time, far from being complete and systematic.

In the present work, a more detailed investigation of the character of the absorption of light in the ultraviolet region of the spectrum by cyanuric acid derivatives as a function of the pH of the medium has been carried out. On the basis of the experimental data, all the dissociation and basicity constants have been computed, and conclusions concerning the structure of the ions of these compounds in solution have also been drawn.

The synthesis of the preparations employed has been described by us in previous communications.[4, 5] The spectra were measured with the help of an SF-4 quartz spectrophotometer in buffer solutions consisting of substances transparent in the ultraviolet region. Immediately before the spectra were taken, the pH value of the solution was measured using an LP-5 vacuum-tube potentiometer with a glass electrode. The temperature at the moment of measurement varied between the limits of 20 and 23°C.

In the study of the absorption spectra in strong acids and alkalies, solutions 0.1 N, 0.5 N, 1 N, 2 N, 3 N, 4 N, 5 N, 7 N, 8 N, and 10 N in hydrochloric acid and 0.1 N, 0.5 N, 1 N, and 2 N in KOH were used. The negative logarithms of the effective hydrogen-ion concentrations were found with the help of the activity coefficients[6] for all the above-named solutions.

Cyanuric acid (2,4,6-trihydroxy-s-triazine) and its derivatives—ammelide (2,4-dihydroxy-6-amino-s-triazine), ammeline (2-hydroxy-4,6-diamino-s-triazine), and melamine (2,4,6-triamino-s-triazine)—possess clearly-marked acid-base properties, which manifest themselves in the relative ease with which these substances form

salts in which they act as acids and bases. The acidic properties of the sequence cyanuric acid, ammelide, ammeline, melamine diminish sharply from cyanuric acid to melamine. Ammelide and ammeline, which have both amino and hydroxy groups in the make-up of their molecules, possess amphoteric properties, forming salts both with acids and with alkalies.

The structure of the crystalline salts of cyanuric acid derivatives acting as acids and bases, and their preparation, have been described by us in reference 7. In the work cited, it was shown that the neutral compound and the ion corresponding to it have different structures with different distributions of multiple bonds in the molecule. In solution, along with the shift of the molecular-ionic equilibrium with change in pH, the value of the absorption coefficient will evidently change also.

In Figs. 1 and 2 are presented the dependence of the molar absorption coefficients on the pH of solutions of cyanuric acid derivatives. The dependences presented appear as stepwise curves, with portions in which the molar absorption coefficient does not depend on the pH of the solution. These portions are related to the regions in which only one of the forms of the molecular-ionic equilibrium exists.

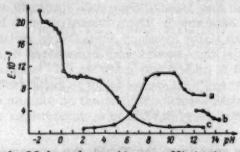
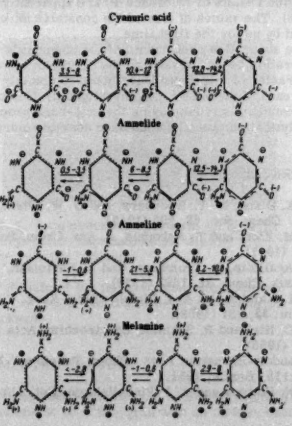


Fig. 1. Molar absorption coefficients of cyanuric acid and melamine at various pH. Curve a—cyanuric acid (λ = 220 mμ); curve b—the same (λ = 230 mμ); curve c—melamine (λ = 236 mμ).

Taking account of the results of references 7 and 8, in which the structure of the molecular and ionic forms of cyanuric acid derivatives was established, we can represent the molecular-ionic equilibria[9] in the following way:



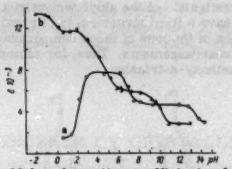


Fig. 2. Molar absorption coefficients of ammeline and ammelide at various pH. Curve a—ammelide (λ = 226 mμ); curve b—ammeline (λ = 230 mμ).

In Figs. 3-6 are presented the absorption spectra of the substances studied, in those pH intervals where only equilibrium form exists. From the figures it can be seen that each equilibrium form has its own characteristic absorption spectrum, distinguished by both the magnitude of the absorption coefficient and the position of the band maximum.

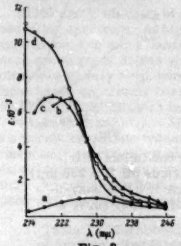


Fig. 3

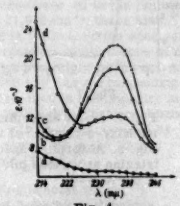


Fig. 4.

Fig. 3. Absorption spectra of cyanuric acid at various pH. pH values: curve a—2, curve b—14.3, curve c—12, curve d—8.8.
Fig 4. Absorption spectra of melamine at various pH. pH values: curve a—11.6, curve b—(–2), curve c—(–1), curve d—2.1.

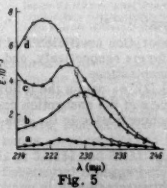


Fig. 5

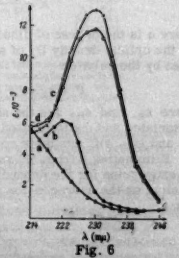
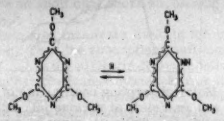


Fig. 6

Fig. 5. Absorption spectra of ammelide at various pH. pH values: curve a—0.5, curve b—14.2, curve c—9.3, curve d—4.6.
Fig. 6. Absorption spectra of ammeline at various pH. pH values: curve a—11.8, curve b—8.1, curve c—1.3, curve d—(–1.1).

The investigation of the alkyl derivatives of cyanuric acid, which have a fixed structure, is of great interest. The formation of the ions of these compounds takes place without any rearrangements. Thus, for example, in the case of trimethoxy-s-triazine



The ionization of trimethoxy-s-triazine takes place only by virtue of the basicity of the s-triazine ring.

Figures 7 and 8 show the dependence of the absorption coefficient of trimethoxy-s-triazine on the pH of the solution, and the absorption spectra of its equilibrium forms.

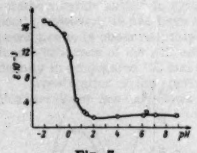


Fig. 7

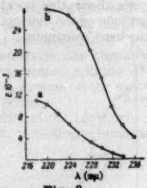


Fig. 8

Fig. 7. Molar absorption coefficient of trimethoxy-s-triazine at various pH (λ = 230 mμ).
Fig. 8. Absorption spectra of trimethoxy-s-triazine at various pH. pH values: curve a—2, curve b—4.

In the case of a monobasic acid (or base), dissociating according to the scheme

$$HR \rightleftarrows R^- + H^+,$$

the dependence of the absorption coefficient ε of the solution on the hydrogen-ion concentration $[H^+]$ may be obtained by using the expression for the dissociation constant

$$K = \frac{[H^+]\alpha}{1-\alpha}, \qquad (1)$$

where α is the degree of dissociation, and the expression for the optical density D_λ of a two-component system is given by the relation

$$D_\lambda = \varepsilon_{R^-}\alpha C + \varepsilon_{HR} C(1-\alpha), \qquad (2)$$

where ε_{R^-} and ε_{HR} are the absorption coefficients of the dissociated and undissociated forms respectively, and αC and $(1-\alpha)C$ are their concentrations.

Eliminating α from (1) and (2), we obtain the following expression for the dependence of the absorption coefficient on the hydrogen-ion concentration in the solution:

$$\varepsilon = \frac{\varepsilon_{R^-} - \varepsilon_{HR}}{1 + \frac{[H^+]}{K}} + \varepsilon_{HR}. \qquad (3)$$

From Eq. (3) it can be seen that, for $[H^+] \gg K$ or $[H^+] \ll K$, ε does not depend on the hydrogen-ion concentration; this situation corresponds to the existence of only one of the equilibrium forms. For $[H^+] = K$, we have

$$\varepsilon = \frac{\varepsilon_{R^-} + \varepsilon_{HR}}{2}. \qquad (4)$$

Expression (4) may be used to determine the dissociation constants. Equation (3) may also be generalized to the case of polybasic acids (or bases), when the dissociation constants differ greatly from one another:

$$\varepsilon = \varepsilon_{n+1} + \sum_{i=1}^{n} \frac{\varepsilon_i - \varepsilon_{i+1}}{1 + \frac{[H^+]}{K_i}}, \qquad (5)$$

where n is the basicity of the acid and ε_i are the absorption coefficients of the separate molecular-ionic forms.

In the Table are presented the values of the dissociation and basicity constants of the compounds investigated, found according to formula (4). For comparison, the available literature data are presented in a separate column.

Compound	Basicity and acidity constants	
	Our data	Literature data
Melamine	$K_{b1} = 1.26 \cdot 10^{-9}$ $K_{b2} = 1.58 \cdot 10^{-14}$ $K_{b3} = 10^{-17}$	$K_{b1} = 10^{-8}$ [1]; $K_{b1} = 1.27 \cdot 10^{-9}$ [2] $K_{b2} = 10^{-14}$ [1] —
Ammeline	$K_{b1} = 5.01 \cdot 10^{-10}$ $K_{b2} = 3.97 \cdot 10^{-13}$ $K_{a1} = 1.26 \cdot 10^{-10}$	$K_{b1} = 3.15 \cdot 10^{-10}$ [2] — $K_{a1} = 4 \cdot 10^{-10}$ [2]
Ammelide	$K_{b1} = 6.3 \cdot 10^{-13}$ $K_{a1} = 10^{-7}$ $K_{a2} = 3.98 \cdot 10^{-14}$	$K_{b1} = 1.57 \cdot 10^{-13}$ [2] $K_{a1} = 1.02 \cdot 10^{-7}$ [2] $K_{a2} = 3 \cdot 10^{-14}$ [2]
Cyanuric acid	$K_{a1} = 6.3 \cdot 10^{-7}$ $K_{a2} = 7.94 \cdot 10^{-11}$ $K_{a3} = 3.16 \cdot 10^{-14}$	$K_{a1} = 1.8 \cdot 10^{-8}$ [10]; $K_{a1} = 4.0 \cdot 10^{-7}$ [2] $K_{a2} = 3.8 \cdot 10^{-12}$ [2] —
Trimethoxy-s-triazine	$K_{b1} = 1.6 \cdot 10^{-14}$	—

As can be seen from the Table, the agreement of the available literature data with those obtained in the present work for melamine may be considered satisfactory. Satisfactory agreement is also to be noted for K_{b1} of ammeline and K_{a1} and K_{a2} of ammelide. Less satisfactory agreement with the literature data is observed in the cases of K_{a1} of ammeline, K_{b1} of ammelide, and K_{a2} of cyanuric acid. For K_{a1}, we may note the satisfactory agreement with the results of the latest work[8] and the less satisfactory agreement with the data of an earlier work[10] (the results of reference 10 are apparently erroneous). The values of four of the constants have been obtained by us for the first time.

The absorption coefficients of the compounds under consideration depend greatly on the acidity of the medium, the character of this dependence being completely different for each of the substances investigated. This opens wide possibilities of employing the acid-base properties for analytical purposes, as has been done in reference 11.

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THE INFLUENCE OF IMPURITIES ON THE LUMINESCENCE OF CRYSTALLINE NAPHTHALENE

M. T. Shpak and E. F. Sheka

Received 18 September 1959

The influence of temperature and impurity concentration on the luminescence and absorption spectra of solutions of β-methylnaphthalene, α-methylnaphthalene, β-naphthol, and α-naphthol in crystalline naphthalene was investigated.

A number of effects were discovered, showing that molecules of β- and α-methylnaphthalene, and also β- and α-naphthol, form two types of luminescence centers when they are introduced into the crystalline lattice of naphthalene.

In reference 1 it was shown that the well-known luminescence of crystalline naphthalene[2] was caused by an impurity of β-methylnaphthalene. It was also established that crystalline naphthalene contains small amounts of α-naphthol, β-naphthol, thionaphthene, and, apparently, other impurities. Hence the investigation of the influence of the concentration of these impurities and the temperature of the sample on the luminescence spectrum of crystalline naphthalene is of considerable interest.

EXPERIMENTAL METHOD*

*E. G. Ruseva, diplomantka KGU, took part in the experimental section of the work.

The experimental method was described previously in reference 3. Crystals of chemically pure naphthalene, purified by recently developed zone refining technique,[4] were used as original samples. It should be noted that we were unable to purify the naphthalene completely. The luminescence spectrum of the original substance is shown in Fig. 1.

Fig. 1. Luminescence spectrum (at 20.4°K) of crystalline naphthalene purified by the zone refining technique.

An estimate of the impurity concentration was made from the absorption spectra of monocrystals of the same thickness.

EXPERIMENTAL RESULTS

The luminescence spectrum of β-methylnaphthalene in naphthalene at 20.4°K begins with an intense band at $\nu = 31060$ cm^{-1}, which is in resonance with a band in the absorption spectrum. At high concentrations of β-methylnaphthalene, two more bands are observed in the luminescence spectrum at 31,044 and 31,016 cm^{-1}; these also coincide with very weak bands in the absorption spectrum. These bands apparently correspond to combinations of an electronic transition with lattice vibrations of the solvent. If we take the band at $\nu = 31,060$ cm^{-1} as corresponding to a purely electronic transition, then in the impurity luminescence spectrum we can isolate ten vibrational bands whose frequencies agree well with the data obtained by others,[3, 5] and also with the frequencies in the Raman spectra of β-methylnaphthalene[6] (Table 1).

Table 1. Vibrational Frequencies (in cm^{-1}) of the Unexcited State of β-Methylnaphthalene in Crystalline Naphthalene at 20.4°K (High Concentration)

$\nu_0 = 31060 \pm 10$			$\Delta\nu_{Raman}$ (ref. 6)
$\Delta\nu$	$\Delta\nu$ (ref. 2)	$\Delta\nu$ (ref. 5)	
57 (w)	—	—	—
288 (w)	292 (3)	288	285 (25)
406 (m)	409 (4)	410	408 (49)
517 (s)	519 (8)	520	520 (320)
768 (m)	775 (6)	775	771 (650)
948 (m)	954 (4)	954	952 (35)
1031 (w)	1021 (3)	1022	1023 (180)
1388 (s)	1379 (8)	1380	1380 (1750)
1581 (w)	1583 (2)	—	1578 (190)
1636 (w)	1632 (3)	—	1634 (25)

Note. In this and the following tables we enclose in parentheses the relative intensities of corresponding bands in the luminescence and Raman spectra using the arbitrary units adopted in the references cited (see also the second footnote to this text).

In the absorption spectrum of β-methylnaphthalene in naphthalene at 20.4°K, there are fourteen weakly polarized bands which are separated from the band at $\nu = 31060$ cm^{-1} by the following intervals: $\Delta\nu$: −48, −19, 47, 94, 177, 194, 209, 221, 250, 282, 331, 687, and 720 cm^{-1}. The bands corresponding to these vibrations (except the bands at 31,154 and 31,310 cm^{-1}) are very weak.

Substantial changes take place in the luminescence spectrum of β-methylnaphthalene when its concentration is decreased. In the spectra of extremely pure samples there is a band at 31,479 cm^{-1} which is polarized in the a direction.[4] The band at 31,060 cm^{-1} and those serially connected with it are considerably weakened. At the same time, the series beginning with the band at 30,972 cm^{-1}, which in the spectra of β-methylnaphthalene at high

concentration was very weak (Fig. 1), has become stronger. In this series one can isolate seven vibrational frequencies ($\Delta\nu$ = 252 (m), 511 (m), 635 (w), 760 (m), 1113 (w), 1190 (w), and 1381 (s) cm^{-1}).* When the temperature of the samples is increased, significant changes in the luminescence spectra occur only in the region of the exciton bands.[4] The spectrum of the impurity luminescence becomes more diffuse.

*Conventional symbols for intensities: w—weak, m—medium, s—strong.

A very weak and narrow band at ν = 31085 cm^{-1} is observed in the absorption spectra of thick monocrystals of naphthalene (d ~ 5-7 mm), carefully purified by the zone refining technique. It has the same intensity as the band at 31,060 cm^{-1}. In all probability, the band at 31,085 cm^{-1} belongs to some unknown impurity.

In the usual preparations of naphthalene, α-methylnaphthalene is not detected. At 20.4°K, the absorption and luminescence spectra of naphthalene saturated with α-methylnaphthalene (the solubility of α-methylnaphthalene in naphthalene is limited) show resonant coincidence of four bands, one of which belongs to β-methylnaphthalene; the second is a series beginning at 31,972 cm^{-1}. However, the relative intensities of these two bands in the luminescence spectrum of naphthalene containing α-methylnaphthalene differ markedly from the intensities of the corresponding bands in the spectrum of the original sample (Fig. 1) and are similar to the distribution of intensities in the luminescence spectrum of naphthalene with a high β-methylnaphthalene content. In all probability, this fact is connected with the presence of β-methylnaphthalene as an impurity in α-methylnaphthalene (the same distribution is not observed in the spectrum of α-methylnaphthalene in a free crystal of naphthalene*

*In the other cases, the impure crystals were grown in quartz vessels.[3]

that has been exposed to vapors of α-methylnaphthalene for several hours). This is confirmed by the fact that even in absorption spectra of naphthalene containing α-methylnaphthalene, the bands of β-methylnaphthalene are very intense, whereas in the absorption spectrum of a control sample twenty times as thick as the sample containing the impurity, these bands were generally absent. The remaining resonantly coincident bands in the luminescence spectrum have the frequencies 31,252 and 30,896 cm^{-1}; the second band being markedly weaker than the first. If we start with these bands, then two series of bands can be distinguished in the luminescence spectrum. The vibrational frequencies of these series are presented in Table 2. The frequencies of these series coincide within the errors of measurement. Thus the luminescence spectrum of α-methylnaphthalene in naphthalene at 20.4°K consists of two identical spectra displaced relative to one another by the constant interval $\Delta\nu$ = 355 cm^{-1}.

Table 2. Vibrational Frequencies (in cm^{-1}) of the Unexcited State of α-Methylnaphthalene in Naphthalene at 20.4°K

ν_0 = 31252	ν_0 = 30896	$\Delta\nu_{Raman}$ (ref. 7)
$\Delta\nu$	$\Delta\nu$	
30 (c)	—	—
103 (c.s.)	—	—
517 (c)	512 (c)	513 (4)
1022 (c.p.)	—	1023 (5)
1390 (c)	1380 (c.p.)	1375 (10)
1476 (c.s.)	1465 (c.s.)	1466 (4)

As the sample temperature increases to 77°K, the series beginning at 31,252 cm^{-1} disappears completely from the luminescence spectrum (Fig. 2), and the bands of the series starting at 30,896 cm^{-1} begin to fade out. It is interesting to note that in the presence of α-methylnaphthalene, the bands of β-methylnaphthalene preserve their sharpness even in spectra of samples taken at 200°K (Fig. 2). No concentration dependence is detected in the spectra of solutions of α-methylnaphthalene in naphthalene.

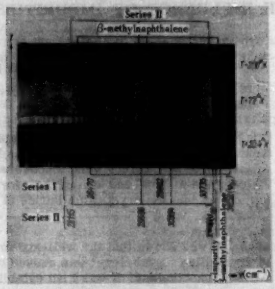

Fig. 2. Luminescence spectra of a trace of α-methylnaphthalene in crystalline naphthalene at various temperatures.

The absorption spectrum of β-naphthol in naphthalene at 20.4°K consists of more than forty narrow bands. In the long wavelength region of the spectrum there are two intense bands with frequencies of 29,944 and 30,081 cm^{-1}, which coincide resonantly with bands from the luminescence spectrum. In the luminescence spectrum these bands begin two identical series (displacement $\Delta\nu$ = 137 cm^{-1}), the vibrational frequencies of which agree with each other and with frequencies obtained from the Raman spectrum of β-naphthol[7] (Table 3.). When the concentration of β-naphthol in naphthalene was increased, the luminescence spectrum of the original sample first weakened, and then disappeared altogether. At very high concentrations, the series beginning at 30,081 cm^{-1} disappeared (Fig. 3).

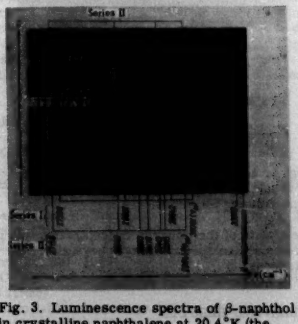

Fig. 3. Luminescence spectra of β-naphthol in crystalline naphthalene at 20.4°K (the vertical arrow indicates the direction of increasing concentration of β-naphthol in the specimens).

In the absorption spectrum of β-naphthol in naphthalene, it is also possible to isolate two series of bands with very similar vibrational frequencies ($\Delta\nu$ = 297, 406, 503 cm^{-1} in the series beginning at 29,944 cm^{-1} and $\Delta\nu$ = 313, 405, 505 cm^{-1} in the series beginning at 30,081 cm^{-1}).

As the temperature is increased, the series beginning at 30,081 cm^{-1} becomes more intense in the luminescence spectrum. The entire spectrum is displaced toward the blue, and the bands become weaker.

In the luminescence spectrum of α-naphthol in naphthalene at 20.4°K (Fig. 4) there are two intense bands at

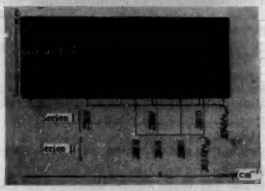

Fig. 4. Luminescence spectra of α-naphthol impurity in crystalline naphthalene at 20.4°K (the vertical arrow indicates the direction of increasing concentration of α-naphthol in the specimens).

30,746 and 30,370 cm^{-1}, which resonantly coincide with corresponding absorption bands. These bands are the initial members of two similar series (displacement $\Delta\nu$ = 376 cm^{-1}), the vibrational frequencies of which are given in Table 4. Increasing the concentration of α-naphthol in naphthalene leads to a complete quenching of the luminescence of the original preparation. With increasing sample temperature the luminescence spectrum of α-naphthol in naphthalene fades away. At the same time, the short wavelength bands are substantially weakened.

Table 3. Vibrational Frequencies (in cm^{-1}) of the Unexcited State of β-Naphthol in Naphthalene at 20.4°K

ν_0 = 30081	ν_0 = 29944	$\Delta\nu_{Raman}$ (ref. 7)
$\Delta\nu$	$\Delta\nu$	
46 (m)	49 (s)	—
299 (m)	268 (m)	—
354 (m)	354 (w)	350 (1)
439 (s)	429 (s)	428 (2)
486 (w)	468 (s)	466 (3)
527 (m)	529 (s)	527 (4)
717 (m)	727 (w)	—
777 (m)	774 (s)	769 (5)
820 (w)	821 (m)	822 (1)
—	957 (s)	924 (0)
991 (w)	992 (w)	—
1046 (m)	1051 (m)	1063 (1)
1156 (w)	—	—
—	1185 (m)	1177 (1)
1292 (w)	1297 (m)	—
1394 (s)	1395 (s)	1386 (7)
1435 (s)	1434 (w)	—
1471 (w)	1476 (m)	1473 (4)

Table 4. Vibrational Frequencies (in cm^{-1}) of the Unexcited State of α-Naphthol in Naphthalene at 20.4°K

ν_0 = 30746	ν_0 = 30370	$\Delta\nu_{Raman}$ (ref. 7)
$\Delta\nu$	$\Delta\nu$	
50 (m)	45 (m)	—
—	280 (m)	271 (2)
473 (m)	469 (s)	471 (6)
526 (m)	522 (m)	528 (4)
575 (m)	574 (m)	574 (5)
712 (w)	718 (m)	713 (7)
—	955 (s)	—
—	1079 (m)	1083 (4)
1146 (w)	—	1141 (4)
—	1169 (w)	—
1207 (w)	—	—
—	1218 (w)	—
1256 (w)	1264 (w)	1246 (5)
1396 (s)	1392 (s)	1377 (10)
1693 (w)	1691 (w)	—

Special investigations were conducted in order to clarify the mechanism of formation of β- and α-naphthol in naphthalene. Powdered naphthalene was submitted to the action of ozone and ultraviolet light from a high voltage spark for several minutes. Figure 5 shows the absorption spectrum of a crystal of naphthalene 300 μ thick that was given this treatment. This spectrum shows very intense absorption bands of β- and α-naphthol,

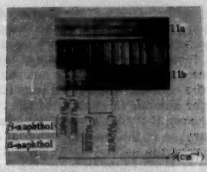

Fig. 5. a and b are the components of the luminescence spectrum of oxidized crystalline naphthalene at 20.4°K.

which are completely absent from the spectrum of the control sample. The absorption bands of β- and α-naphthol are also observed in the spectrum of a thick monocrystal of naphthalene whose surface has been treated in the same manner as the powder. Hydrogen peroxide affects crystalline naphthalene in the same way as ozone and short wavelength radiation.

DISCUSSION OF THE RESULTS

Our basic experimental results reduce to the following: (1) The impurities influence each other's luminescent properties (thus, in the presence of α-methylnaphthalene, the luminescence bands of β-methylnaphthalene in naphthalene remain sharp even at 200°K. (2) The spectra of α-methylnaphthalene, β-naphthol, and α-naphthol in naphthalene at 20.4°K consist of doublets, and in the case of α-methylnaphthalene and β-naphthol the vibrational frequencies of the two components of the spectra coincide within experimental error. (3) In the case of β-naphthol, increasing the concentration of impurity leads to the disappearance from the luminescence spectrum of the short wavelength series of the doublet. (4) Increasing the temperature of the samples leads not only to a fading of the bands in their spectra, but also, in the case of α-methylnaphthalene, to the disappearance of the short wavelength series of the doublet from the luminescence spectrum. (5) In all cases, the luminescence of the original sample disappears upon the introduction of large quantities of impurities into the naphthalene.

At the present time there is no theory which can explain in detail the influence of a crystalline lattice on the spectra of molecules introduced into it. We can therefore attempt only a qualitative explanation of some of these results. In addition, it should be kept in mind that the analysis of the observed phenomenon is made difficult by the fact that in the case of naphthalene we are dealing with not just one impurity, but several. The latter circumstance forces us to conduct all investigations with considerable concentrations of the impurities introduced into naphthalene, under which circumstances the luminescence of the original samples due to residual impurities is suppressed.

The well-defined doublet structure of the spectra investigated can be explained if one assumes that in solutions of α-methylnaphthalene, β-naphthol, and α-naphthol in the crystalline lattice of naphthalene there are formed two types of spatially distributed emission centers which differ from each other, apparently, in the different orientation of the molecules relative to the crystallographic axes of the crystal-solvent[9,10] and by a different degree of deformation. Confirming this we have the resonant coincidence of the initial bands in the absorption and luminescence spectra, and the fact that these centers be-

have differently with changes in the temperature of the samples and in the concentration of the dissolved substance. The centers of one type exert a quenching effect on the other at certain concentrations and temperatures. This concentration quenching may be connected with the fact that when the concentration of an impurity is increased, a larger number of centers of one type are formed. (It is known that in a crystal containing two impurities, an increase in the concentration of one causes the luminescence of the second to die out.) The temperature quenching of luminescence indicates that the role of radiationless transitions becomes more important as the temperature is increased. It is necessary, however, to keep in mind that along with this the natural luminescence of the crystal may be triggered.[4]

In the light of what was said above, it is possible to regard the spectrum of β-methylnaphthalene as a doublet also, the series beginning at 30,972 cm^{-1} serving as the second component. The difference between the present case and the preceding ones is that in the absorption spectra of even the thickest crystals of naphthalene, the bands which should coincide resonantly with this band are not observed. Besides, the vibrational frequencies of the two indicated spectra differ more from each other than in the other cases considered in this paper.

Starting from general principles of organic crystal-chemistry and considering the influence of the symmetry of molecular crystals on solid solution formation, Kitaigorodskii[11, 12] came to the conclusion that upon the introduction into a crystal-solvent of solute molecules having a lower symmetry than the molecules of the solvent, two cases are possible: (1) the molecules of the dissolved substance will imitate the symmetry of the solvent molecules, and (2) the molecules of the dissolved substance will not imitate the symmetry of the arrangement of molecules in the solvent (in this case the crystal-solvent lowers its symmetry with the entry of molecules of the dissolved substance.) Since the preservation of a high degree of symmetry is energetically profitable, the first possibility is realized in all cases in which the molecules of the solute are able to imitate the symmetry of the molecules of the crystal-solvent. Molecules of β-methylnaphthalene, α-methylnapthalene, β-naphthol, and α-naphthol do not possess centers of symmetry with regard to inversion, whereas the naphthalene molecule does; but two molecules of each of these substances can always be oriented in such a fashion that a center of symmetry with regard to inversion shows up between them. If molecules of the substances mentioned are introduced into the naphthalene lattice in the same fashion, then it is possible that the separate centers of luminescence appear as complicated complexes of molecules.

In conclusion, we express our thanks to A. F. Prikhot'ko for his interest in the work and for valuable discussions.

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LIGHT ABSORPTION AND LUMINESCENCE OF M-CENTERS IN A MACROSCOPIC APPROXIMATION

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Pekar[1-3] has developed a macroscopic theory of F-centers in ionic crystals which permits calculation of the energy levels and wave functions of the F-centers and the determination of the absorption band and luminescence parameters. Besides F-centers, there are more complex color centers in colored crystals. It is entirely possible for centers to be formed which represent a combination of an F-center with a pair of nearby vacancies. According to Seitz[4], such centers ought to be responsible for the M-band observed in the spectra of colored alkali halide crystals.

In the present paper we calculate, in a macroscopic approximation, the absorption band and luminescence parameters for the M-center model.[4]

The calculation was performed exactly as described in references 5-7. The Hamiltonian of the crystal color-center system is the sum of the operators for the kinetic energy of the color-center electron, the electrostatic interaction between the electron and the vacancies and of the vacancies among themselves, the interaction energy of the electron with the crystal, and the energy of the crystal lattice vibrations. The periodic part of the potential is excluded by the use of the effective mass method. In the adiabatic approximation, the system is divided into vibrational and electronic subsystems. The energy and basic function of the ground state of the electronic subsystem are determined by the variational method, taking into account the symmetry properties of the color center.

The investigation conducted in references 5 and 6 shows that the form of the electronic wave function of the ground state of the aggregate color center depends significantly on the crystal parameters. Hence, the determination of the parameters corresponding to the absorp-

tion bands and luminescence is conveniently accomplished by assigning concrete values to the crystal parameters. We chose the crystal KCl—a typical representative of the alkali halides. This choice is explained by the fact that alkali halide crystals are apparently the only group of crystals for which sufficiently reliable measurements have been made of the physical quantities appearing as parameters in the theory, and for which the absorption spectra of the aggregate color centers have been studied.

A disadvantage of the choice we have made is the circumstance that the criterion of applicability of the macroscopic approximation to the consideration of color centers in alkali halide crystals is achieved in the limit.[3, 5, 6] The numerical values of the absorption band and luminescence parameters obtained in the macro-approximation are therefore only approximate.

The determination of the electronic part of the wave function of the ground state of the M-center is based on a knowledge of the corresponding wave functions of F_2^+- and F^--centers which represent the combination of an F-center with vacancies of negative and positive ions respectively. These wave functions were derived in references 5 and 6. The approximate wave function for an F_2^+-center was chosen in reference 5 in the form

$$\psi(r) = \psi_a(r) + \gamma\psi_b(r),$$

where ψ_a and ψ_b are wave functions of the F-center type (the values of γ were determined by the variational method). The energy and wave function of the ground state of the F_2^+-center were determined in reference 5 as functions of the separation R between the vacancies which constitute the F_2^+-center. For small values of R, γ becomes equal to unity; with increasing R the value of γ sharply decreases, tending toward zero as R goes to infinity. Practically speaking, $\gamma \approx 0$ when R is of the order of the lattice constant.

Thus, within the approximations used, the wave function of the ground state of the F_2^+-center in alkali halide crystals practically coincides with the wave function of the F-center.

Starting with the result obtained, we undertook a macroscopic treatment of the F_2^--center in alkali halide crystals with the help of the variational method, leaving the confines of the adiabatic approximation; the approximate wave function of the ground state was chosen in the form

$$\psi = \psi_a(r)\,\Phi(q_x - q^0_{x,a}) + \psi_b(r)\,\Phi(q_x - q^0_{x,b}),$$

where Φ is the wave function of the oscillator subsystem in the adiabatic approximation, q_x are the normal coordinates, and $q^0_{x,a}$ and $q^0_{x,b}$ are the coordinates of the equilibrium positions of the nuclei for the cases in which, for the adiabatic treatment, the electronic part of the F_2^--center wave function is equal respectively to ψ_a and ψ_b.

Calculation shows that the overlap integrals constructed on the functions $\psi_a(r)\Phi(q_x - q^0_{xa})$ and $\psi_b(r)\Phi(q_x - q^0_{xb})$ are small, and the energy of the system computed by this method coincides with the energy obtained in the adiabatic approximation. Consequently, for the treatment of F_2^--centers in alkali halide crystals it is possible to make use of the wave function obtained in the adiabatic approximation with the very same justification as is used when the wave function for the H_2^+ molecule is identified with the wave function of a hydrogen atom for large nuclear separations.

As is shown in reference 6, the wave function of the ground state of an F^--center in the case of alkali halide crystals also differs little from the wave function of an F-center.

These results permit the approximate replacement of the wave function of the ground state of an M-center in alkali halide crystals by the wave function of an F-center. As a zeroth approximation to the excited states of the M-center, let us consider the wave equation for the F-center

$$[T_e + Q + V]\,\varphi_i(r) = E_i\varphi_i(r), \tag{1}$$

where T_e is the kinetic energy of an electron with effective mass μ, V is the energy of interaction of the electron with the polarization set up by the ψ-cloud of the electron in the ground state, and Q is the energy of interaction of the electron with the F-center vacancy denoted by a.

We shall consider as a perturbation the expression

$$W = \frac{e^2}{\varepsilon}\left(\frac{1}{R_{ab}} - \frac{1}{R_{ac}} - \frac{1}{r_b} + \frac{1}{r_a}\right), \tag{2}$$

where b and c refer to the vacancies of negative and positive ions, respectively, R_{km} is the separation between vacancies k and m, r_k is the distance between the electron and vacancy k, and ε is the dielectric constant. Taking into consideration the four lowest excited levels of the F-center with close eigenvalues E_i^0, we obtain the following expression for the excited levels of the M-center, in the first approximation of the perturbation theory

$$E_{1,2} = \frac{1}{2}\left(E_1^0 + E_2^0 + W_{11} + W_{22}\right) \mp \sqrt{\frac{1}{4}\left(E_1^0 - E_2^0 + W_{11} - W_{22}\right)^2 + W_{12}^2 + W_{23}^2};$$

$$E_3 = E_4 = E_1^0 + W_{11}; \tag{3}$$

$$\psi_s = \frac{W_{12}}{\left[W_{12}^2 + W_{23}^2 + \left(E_1^0 + W_{11} - E_s\right)^2\right]^{1/2}} \cdot \left[\psi_1^0 - \frac{E_1^0 + W_{11} - E_s}{W_{12}}\psi_2^0 + \frac{W_{23}}{W_{12}}\psi_3^0\right], \quad s = 1, 2; \tag{4a}$$

$$\psi_{3,4} = \frac{W_{23}}{\sqrt{2\left(W_{12}^2 + W_{23}^2\right)}}\left[\psi_1^0 - \frac{W_{12}}{W_{23}}\psi_3^0 \mp \frac{\sqrt{W_{12}^2 + W_{23}^2}}{W_{23}}\psi_4^0\right], \tag{4b}$$

where W_{ik} is a matrix element of W derived from the wave functions ψ_i^0:

$$\psi_1^0 = \beta^{3/2}\pi^{-1/2}e^{-\beta r}\cos\vartheta; \quad \psi_2^0 = \delta^{3/2}\pi^{-1/2}\left(\beta^3 - 3\rho\beta + 3\rho^2\right)^{-1/2}(1 - \rho r)\,e^{-\delta r};$$

$$\psi_3^0 = \beta^{3/2}\pi^{-1/2}\exp(-\beta r)\,r\sin\vartheta\cos\varphi; \quad \psi_4^0 = \beta^{3/2}\pi^{-1/2}e^{-\beta r}r\sin\vartheta\sin\varphi.$$

β and δ are approximation parameters, and ρ is determined from the condition that the function ψ_2^0 be orthogonal to the ground-state wave function of the F-center.

The frequencies of the absorption band maxima are determined from the formula $\hbar\Omega_{0m} = |E_0 - E_m|$; the oscillator strength corresponding to a phototransition is given by

$$f_{km}^x = \frac{2\mu}{\hbar^2}\hbar\Omega_{km}x_{km}^2,$$

where x_{km} is a matrix element of x, which is a component of the radius vector of the electron.* In particular,

*As is well known,[8] the relation $\sum_m f_{km}^x = 1$ holds for the f_{km}^x.

in agreement with the formulas (4),

$$z_{si} \sim \cos\vartheta + \lambda\sin\vartheta\cos\Phi \quad (i = 1, 2); \tag{5}$$

$$z_{si} \sim \cos\vartheta - \frac{1}{\lambda}\sin\vartheta\cos\Phi \mp \frac{1}{\lambda}\sqrt{1 + \lambda^2}\sin\vartheta\sin\Phi \quad (i = 3, 4), \tag{6}$$

where $\lambda = W_{23}/W_{12}$. The double sign in (6) corresponds

to the two possible locations of the vacancy at the M-center with respect to the given locations of the vacancies a and b (θ and Φ are the angles between the axis ab of the M-center and the z-axis).

We shall employ the results obtained for a quantum-mechanical interpretation of experiments on polarized luminescence of colored crystals.[13] Suppose a plate is cut from the crystal, such that its front face is parallel to the (100) crystal plane, and then the crystal is exposed to light which is polarized in this plane. The angle between the direction of the electric field vector E, taken along the z axis, and the direction (001) will be denoted by α. It is not difficult to obtain the dependence of z_{pi} on α for various orientations of the axis ab of the M-center, by expressing the angles θ and Φ in terms of α. We then compute the number of M-centers excited as a result of the exposure (proportional to z_{pi}^2) for each of the orientations of the ab axis which are possible in the crystal. The probability of the emission of light by an excited M-center in a direction perpendicular to the cut face, with an arbitrary polarization, is determined to within a constant factor by means of an integration with respect to α of the square of the matrix element z_{pi}^2. Finally, we determine the values of the partial intensities I_i and the degrees of polarization p, of the radiation for each group of identically oriented M-centers, and the degree of polarization of the emission

$$p = \frac{\Sigma p_i I_i}{\Sigma I_i}.$$

When a phototransition of the electron takes place to the level i = 1 or i = 2, the calculation leads to the following value of p_i:

$$p^+ = \frac{2(1-\lambda^2)^2 - (1-2\lambda^2)\cos^2 2\alpha}{3+8\lambda^2+6\lambda^4}. \qquad (7)$$

If the electron is excited to the level i = 3, 4, but emission occurs from the lowest level i = 1, we have

$$p^- = -\frac{2(1-\lambda^2)^2 - (1-2\lambda^2)\cos^2 2\alpha}{5+12\lambda^2+6\lambda^4}. \qquad (8)$$

The results obtained are also easily explained in terms of the classical theory of absorbing and radiating oscillators. Let us rotate the coordinate system and select values of the direction cosines of the new coordinate axes x′, y′, and z′ such that the following conditions will be achieved in the new coordinates:

$$z_{pi}^2 \sim \cos^2\theta' \ (i=1,\ 2); \quad z_{pi}^2 \sim \sin^2\theta' \ (i=3,\ 4). \qquad (9)$$

It can be shown that the conditions (9) are fulfilled if

$$\cos xy' = \cos yx' = \cos yz' = \cos zy' = 0; \quad \cos yy' = 1;$$
$$-\cos xx' = \cos zz' = \frac{1}{\sqrt{1+\lambda^2}}; \qquad (10)$$
$$\cos xz' = \cos zx' = \frac{\lambda}{\sqrt{1+\lambda^2}}.$$

In this way a crystal containing M-centers can be identified with a collection of classical σ-oscillators (oriented, however, not along the ab axes of the M-centers, but along axes which make angles with them that are determined from Eqs. (10))—or with a set of π-oscillators distributed in planes perpendicular to these new axes.

We note that the azimuthal dependences of the degree of polarization of the M-centers is very close in character to the azimuthal dependences for F_2^- and F_2^+-centers whose symmetry axes coincide with the ab axes of the M-centers. It follows from (5) and (6) that as $\lambda \to 0$, these dependences coincide identically. According to (7), (8), the calculations of Feofilov, and also reference 7, for $\lambda \neq 0$, the azimuthal dependences have the same character (the minima and maxima of $p(\alpha)$ coincide), but the absolute magnitude of p in the case of M-centers differs from that for F_2^- and F_2^+-centers. Thus it becomes possible to distinguish the optical spectra of F_2^- and F_2^+-centers from those of M-centers by means of the azimuthal dependence of the degree of polarization of the radiation.

The results of a numerical calculation for the KCl crystal are presented in the Table.

i	E_i (ev)	φ_i	$\Delta\omega_i$ (ev)	f_{0i}^x	f_{0i}^y	f_{0i}^z
1	−1.46	$0.20\,(\varphi_1^0 - 3.5\varphi_2^0 - 3.6\varphi_3^0)$	1.93	0	0.28	0.02
2	−1.10	$0.17\,(\varphi_1^0 + 4.4\varphi_2^0 - 3.6\varphi_3^0)$	2.29	0.27	0	0.02
3,4	−1.30	$0.68\,(\varphi_1^0 + 0.27\varphi_2^0 \pm 1.0\varphi_3^0)$	2.09	0.04	0.54	0.54

The experimental value of the frequency of the maximum absorption in the M-band in the KCl crystal is 1.5 ev. Thus the result produced by calculation on the Seitz model of M-centers does not agree well with experimental data.

This disagreement is apparently due, in large part, to the aforementioned unfortunate choice of alkali halide crystals as objects for macroscopic consideration of color centers. It is true that in the case of F-centers, the macro-approach leads to an agreement between the results of theory and experiment even in alkali halide crystals. However, the errors brought in by the macroscopic method of calculation increase in the case of complex centers. It is not possible to estimate the magnitude of the errors in the frames of reference applied here. A really rigorous microscopic solution of the problem would involve considerable computational difficulties.

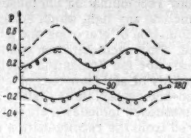
We note that calculation of the frequency of maximum absorption in M-centers on the Seitz model for the KCl crystal using the approximation of a lattice of point ions led to a value of 1.73 ev,[10] whereas the frequency of the F-absorption in the very same approximation equals 2.0 ev,[9] compared to the experimental value of 2.2 ev. The size of the difference between the values of the F- and M-center frequencies calculated in references 9 and 10 (0.3 ev) is much closer to the value of 0.2 ev that we obtained than it is to the experimental value of 0.7 ev. The LCAO method,[11] as indicated by Gourary and Luke,[12] leads to a result close to that obtained by them.

Evidently, none of the methods considered allows one to identify the centers responsible for the bands observed in the spectra with concrete models by means of a comparison between theoretical and experimental values of the frequencies.

However, for the determination of the degree of polarization we used only the general form of the M-center wave functions. The expression found for p depends on the single parameter λ^2 which can be determined not by means of a systematic macro-calculation, but from a comparison of the theoretical and experimental values of $p(\alpha)$ at an arbitrary point α_0, after which the value of λ^2 found will permit calculation of the values of $p^+(\alpha)$ and $p^-(\alpha)$ for arbitrary α. Such a method of calculation will lead to an accurate result even in those cases for which the macro-approximation is not completely correct (it is important only that a qualitatively correct form be found for the wave functions). Hence the consideration of the properties of polarized luminescence brought forward above can be used to identify color centers with concrete models.

We have tried to "recognize" M-centers in NaF by a similar method, using the experimental results of Feo-

filov.[13] According to reference 13, two absorption bands are observed in NaF. Illumination of the crystal with light falling in either region leads to emission in one and the same band, whereas the character of the azimuthal dependence depends on which of the bands is excited. The parameter λ^2 was determined by comparing (7) with the experimental value of p^+ at $\alpha = 0$; $\lambda^2 = 0.12$. In the figure,



the solid lines indicate the results of a theoretical calculation conducted under the assumption that the long wavelength absorption band is caused by a transition to the level $i = 1$ of the M-center, and the short wavelength one to the level $i = 3, 4$. The dashed lines represent the theoretical results for F_A- and F_A^+-centers,[7, 14] the experimental data[13] are plotted as points. As can be seen from the figure, the results of the theory for the case of the M-center are found to be in good agreement with experiment. Therefore the two absorption bands observed in reference 13 must be ascribed to phototransitions of the electron in an M-center. However, inasmuch as the parameter λ^2 was determined empirically, it must be kept in mind that the solution can be nonunique, so that the azimuthal dependence of the type obtained could belong as well to several other complex types of color centers.

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THE MECHANISM OF THE RECOMBINATION LUMINESCENCE OF ACTIVATED ALKALI HALIDE CRYSTALS*

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This paper presents the results of an investigation of recombination luminescence and photochemical transformations in alkali halide crystals activated by the ions Ga^+, Ge^{++}, In^+, Sn^{++}, Tl^+, and Pb^{++}, under excitation by x-rays and light in the exciton and activator absorption band regions, and also in the "zone-zone" bands.

The role of electrons, holes, excitons, and sensitization processes in the recombination emission of phosphors of this class is considered.

At the present time there is no dearth of general theories of the mechanism of the luminescence of solids. However, even for the alkali halide crystals, which have a relatively simple structure, the detailed emission mechanism is not yet clear. Complex investigations of this problem have been conducted in Tartu during the last few years on monocrystals of KCl, KBr, KI, and NaCl activated by gallium, indium, thallium, germanium, tin, and lead.

In references 1 and 2, it was demonstrated spectroscopically that the "heart" of the luminescence centers in this class of crystal phosphors consists of uni- and divalent mercurylike ions of Ga^+, In^+, Tl^+, Ge^{++}, Sn^{++}, and Pb^{++} which, in spite of interaction with the crystalline lattice, retain clear features of similarity to the free ions. The final link in the process leading directly to emission is connected with the change in the electronic state of the mercurylike ions interacting with the neighboring ions of the host lattice (transitions $^3P_1 \rightarrow {}^1S_0$ and $^3P_0 \rightarrow {}^1S_0$). This proved one of the basic hypotheses of the well-known Seitz concept of the mechanism of light emission in the alkali halide crystal phosphors[3] (see also reference 4). The second basic postulate of this concept—the metastable character of the persistent afterglow of activated alkali halide crystal phosphors—proved to be incorrect. The very interesting results of the work of Antonov-Romanovskii[5] and Parfianovich[6] bear witness to this fact, as do all of the experimental data obtained in the last year at Tartu.[7–11] For example, Fig. 1 presents data on the spectra of x-irradiated phosphors KCl-Ga,

KCl-In, KCl-Tl, and KCl-Pb. Characteristically, the emission of the Ga^+, In^+, Tl^+, and Pb^{++} ions arises not only upon excitation in the region of the activator absorption bands (transitions $^1S_0 \rightarrow {}^3P$ and $^1S_0 \rightarrow {}^1P_1$), but also upon excitation in the visible and infrared regions of the spectrum. The maxima in the stimulation of the optical flash for all four phosphors correspond to the absorption bands of color centers in the host substance (F-, M-, N-, and O-centers). The emission spectra of KCl phosphors measured upon excitation in the region of the activator absorption bands, and also upon stimulation of x-irradiated phosphors in the F-band, practically coincide.* In this way, Fig. 1 illustrates the nonmetastability of the persistent phosphorescence of alkali halide phosphors and shows that it is impossible to detect any difference between centers of short-lived and long-lived phosphorescence.

*The difference in the spectra corresponding to the phosphor KCl-Ga is caused by the distorting effect of the reabsorption of the Ga^+ emission by the F-centers.

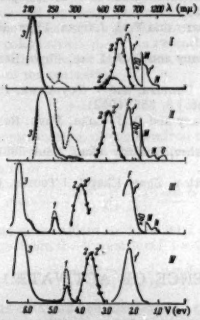

Fig. 1. Excitation spectra (curves 1 and 1′) and emission spectra (curves 2 and 2′) for non-x-irradiated and x-irradiated crystals respectively. (I) KCl-Ga, (II) KCl-In, (III) KCl-Tl, (IV) KCl-Pb; curve 3—absorption spectrum.

The presence of recombination luminescence is a characteristic feature of the crystalline alkali halide luminors possessing poorly mobile point defects in the lattice, which act as effective traps for electrons and holes. In liquid solutions of alkali halide salts and mercurylike ions, where long-range order and stable point-defects are absent, recombination luminescence is not observed, although the intra-center luminescence in many respects suggests the emission of the crystals.[12]

In order to explain the long-time recombination luminescence in crystals, one usually calls upon the notion of the possibility of ionization of the luminescent centers in the excitation process, and the occurrence of emission upon the recombination of the electrons with the ionized centers.[5,7,13] However, in the last year some doubt has arisen[5,14] as to whether the ionization mechanism for long-lived phosphorescence is the only possible one. It is hardly likely that upon excitation of alkali halide phosphors activated by divalent ions, an additional ionization of the already twice-ionized activator particles can take place. Meanwhile, recombination luminescence of Pb^{++} and Mn^{++} ions is certainly observed in x-irradiated KCl-Pb (Fig. 1) and KCl-Mn.* This fact, as well as other data, attests to the insufficiency of the existing hypothesis about the mechanism of recombination luminescence in alkali halide phosphors.[5,14]

In our opinion, the concept of "recombination luminescence" should be given a much broader significance than is usually done. It should not be restricted to the ionization mechanism.

We believe that recombination luminescence of crystals should include any light which arises as a result of the recombination of electrons and holes in the crystalline lattice. This recombination can take place directly on the activator ion (ionization mechanism), in the immediate vicinity of activator ion, or even farther from the luminescence center. In the latter case recombination luminescence includes a stage in which energy is transferred from the recombination center to an un-ionized center of luminescence. The recombination of electrons and holes occurs most frequently when one of the recombination partners is localized. In some cases, emission can also occur upon the recombination of free electrons and holes.

In this connection it is expedient to distinguish the following cases: (1) electronic recombination luminescence (a free electron recombining with a localized hole); (2) hole recombination luminescence (a free hole recombining with a localized electron); and (3) electron-hole recombination luminescence, arising from a recombination of free electrons and holes.

On the basis of this very simple classification, one can raise a question as to the sign of the processes leading to recombination emission in the activated alkali halide crystals. The existence of electronic recombination luminescence is indisputable. It is confirmed, for example, by the data cited above. Emission of the activator ions arises from the photothermal destruction of the F, M, and other centers. Measurements of the sign of the Hall effect and the sign of photoelectric polarization have shown that these are electronic color centers.[15,17] Numerous experiments show that electronic recombination luminescence also arises upon thermal liberation of electrons from the trapping levels.[7,18] In the well-known work of Dutton and Maurer[19] on KCl and KBr, peaks of thermostimulated current were observed. In the opinion of the authors, this was connected with thermal liberation of holes from the V_1 trapping levels, this process being accompanied by a weak thermoluminescence. During the last year a number of attempts have been made at Tartu to detect hole recombination luminescence of activator ions in alkali halide crystals.[8,20-22] The data for the phosphor KCl-In, x-rayed at 100°K, are presented in Fig. 2. Upon heating this phosphor at 100-200°K, a complete decolorization of the hole band at λ_m = 360 mμ and a partial bleaching of the electronic F-band are produced. Along with this, absorption in the region of the V_2-band (λ_m = 232 mμ) increases somewhat. If the rules formulated in references 18 and 20 for determining the sign of electron-hole processes are correct, then the effect under consideration should be interpreted as a result of thermal liberation of holes from trapping levels, followed by recombination with F-centers or relocalization on other hole trapping levels. Figure 2 shows that this process is accompanied by emission from the In^+ ions. At room temperature, the thermoluminescence of KCl-In is without doubt connected with the liberation of electrons from trapping levels, and is thus electronic recombination luminescence.

If hole recombination luminescence of the In^+ ions actually occurs* then a question arises as to the relative roles of these two types of emission in alkali halide

*A direct determination of the sign of thermostimulated current by the dynamic condenser method is necessary.[17]

crystals. Figure 3 presents data for the phosphor KBr-Tl, x-irradiated at low temperature. In the spectrum of excited absorption (curve 1) there are basically two bands: the electronic F-band and the hole band at $\lambda_m = 400$ mμ. In the spectrum of excitation of optical flash of thallium emission (curve 2) the F-band appears with a high yield. The yield of hole recombination luminescence is negligibly small at first glance. However, this is not quite so, inasmuch as analysis of the spectrum of optical bleaching of F-centers[23,24] (curve 3) shows that photothermal liberation of holes from trapping levels is less probable than photothermal liberation of electrons from F-levels. Taking all this into account, we are bound to acknowledge that in the phosphor KBr-Tl, hole recombination luminescence (if it exists!) is less effective than electronic recombination luminescence. An analogous conclusion follows from an analysis of the data on the thermal bleaching of KBr-Tl, as well as KCl-In (Fig. 2).

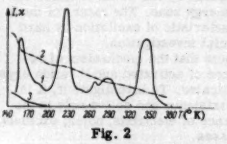

Fig. 2

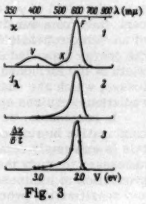

Fig. 3

Fig. 2. Thermoluminescence (curve 1) and thermal bleaching of F- and V_{350}-bands (curves 2 and 3) of KCl-In phosphor, x-irradiated at 100°K (rate of heating β = 0.08 deg/sec).

Fig. 3. Spectra of absorption (1), stimulation of optical flash (2), and optical bleaching of F-centers (3) for the x-rayed phosphor KBr-Tl (temperature of experiment—100°K).

After establishing the sign of the recombination luminescence, it is natural to consider the more detailed features of the mechanism of this emission. Our experiments show that recombination luminescence of alkali halide crystals activated by gallium, indium, and thallium, is excited both in the region of absorption of the luminescence centers and also in the region of the fundamental absorption. The simpler case of excitation of recombination luminescence in the activator absorption bands was studied first of all. Yaek developed several methods of investigating the recombination luminescence excitation spectra, and with their aid studied a series of alkali halide crystals.[10,25] As an example, Fig. 4 shows the data for the phosphors KBr-Ga, KBr-In, KBr-Tl, and KBr-Sn. In KBr crystals activated by univalent mercurylike ions, recombination emission is excited in the region of the activator absorption bands corresponding to the electronic transitions $^1S_0 - {}^1P_1$. In KBr containing divalent Sn^{++} ions it was not possible to excite recombination luminescence in the region of the activator bands. Our experiments showed that to the extent that lowering the temperature hindered excitation of recombination luminescence in the activator absorption bands. Thus, in the excitation of recombination luminescence one doubtless observes a photothermal, and not a purely optical, process.

When alkali halide crystal phosphors are excited by short wavelength ultraviolet radiation, important changes

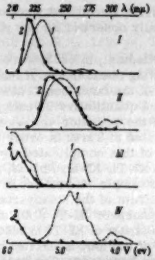

Fig. 4. Spectra of excitation of steady-state luminescence (curves 1) and of recombination phosphorescence (curves 2) for the phosphors KBr-Ga (I), KBr-In (II), KBr-Tl (III), and KBr-Sn (IV).

are observed in their absorption spectra. The spectra of the photochemical action of the ultraviolet radiation spreads out into the region of the "zone-zone" transitions, the region of exciton absorption, and of the absorption band of luminescence centers.[15,26] The changes in the gallium absorption in alkali halide phosphors upon exposure in the region of the gallium absorption bands themselves has been investigated in especial detail.[15] As a result of this action the absorption of the Ga^+ ions decreases, while at the same time F-centers and activator atom centers (Ga^0) are generated. These effects are observed easily at room temperature; however, at 100°K photothermal processes of creation of electronic color centers after optical excitation of the luminescence centers appear to be practically frozen. Further investigations will be necessary in order to explain the detailed mechanism of this process. It could be, for example, a photothermal ionization of the luminescent centers, which is possible in phosphors with univalent activators. In these same phosphors there is observed a decrease in activator absorption, creation of F-centers, and excitation of recombination luminescence upon exposure in the region of the activator absorption bands. For alkali halide phosphors with divalent activators, these effects are not observed, as special experiments have shown. Several other effects which we have observed[10] also agree with the ionization hypothesis (for example, the effect of memory of the site of excitation).

A second possible explanation of the undoubted fact of creation of electronic color centers upon excitation in the region of the activator absorption bands was proposed by one of us.[9] After the excitation of a luminescent center, it is possible, in principle, for there to be a transformation of this localized excitation into a free excitation having three degrees of freedom (the usual exciton) or one degree of freedom ("dislocation exciton"). Later, the free excitation, interacting with various lattice defects, may create electronic and hole color centers. These processes have been specially investigated in references 26 and 27. Recombination luminescence, according to such a mechanism of excitation, can result from a transfer of energy from the recombination centers of electrons and holes (holes and electrons) to unionized centers of luminescence. We have repeatedly tried to detect this theoretically possible type of recombination luminescence. A similar sensitized phorphorescence could explain the presence of hole recombination luminescence and the electronic recombination lumines-

cence of divalent ions. Sensitized phosphorescence of crystals was actually observed for the phosphors $CdBr_2$-Pb, Mn.[28]

Terenin and Klement, in 1935, were the first to describe the interesting phenomenon of luminescence of Tl^+ ions in the region of the fundamental absorption of alkali halide crystals.[29] A quantitative investigation of the excitation spectra of the activator emission of a series of iodides was conducted at Tartu in order to explain the detailed mechanism of this complicated phenomenon.[23,31] (The iodides were KI-Tl, KI-In, RbI-Tl, and CsI-Tl.)

By way of an example we present in Fig. 5 (curve 2) the excitation spectrum of the steady-state luminescence of Tl^+ ions in the phosphor KI-Tl (0.01 mole percent). The absorption spectrum of KI-Tl is also shown (curve 1). The luminescence of the ions is excited not only in the activator absorption bands, but also in the region of the fundamental absorption of KI. Although in the latter case the luminescence yield is almost an order of magnitude less, a very conservative estimate shows that we undoubtedly have here a case of transfer of energy from the host substance to the luminescent centers. The absorption band of KI at $\lambda_m = 219$ mμ corresponds to the creation of excitons in the crystalline lattice of current-less mobile excitations. The results obtained show that, as assumed in reference 23, the excitons being annihilated on luminescence centers transform them into an excited state, as a result of which luminescence occurs.

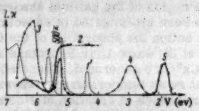

Fig. 5. Spectra of absorption (curves 1, 1'), excitation of steady-state luminescence (curve 2), recombination phosphorescence (curve 3), emission (curve 4), and stimulation of optical flash (curve 5) of a monocrystal of KI-Tl ("optical concentration" of Tl in the crystal 0.01 mole percent).

The exciton mechanism for the excitation of luminescence is not the only one possible, nor is it the most significant. Figure 5 indicates that thallium luminescence is even more effectively excited in the shorter wavelength absorption band, which, according to present theories, corresponds to the "zone-zone" transitions. For the phosphors studied, the electron-hole mechanism of energy transfer to the luminescence centers is more effective than the exciton mechanism. In an additional investigation of electron-hole transfer processes the recombination luminescence (phosphorescence) excitation spectra of a series of iodides was studied in the region of the fundamental absorption.[30] Figure 5 (curve 3) shows the data for the phosphor KI-Tl. It is easy to see that recombination luminescence is relatively weakly excited in the exciton absorption band and very strongly excited in the shorter wavelength region. It is remarkable that the phosphorescence of KI-Tl has a greater yield for the "zone-zone" transitions than for direct excitation of the luminescence centers. Experiments have shown that it is electronic recombination luminescence which is produced when alkali halide crystals are excited in the "zone-zone" region. This follows in a particularly convincing manner from a consideration of Fig. 5, in which curve 5 shows the spectrum of the stimulation of recombination luminescence in KI-Tl after excitation in the "zone-zone" region, coinciding with the F-band absorption of the electronic color centers.

Activator ion luminescence in alkali halide crystals is evoked not only by photoexcitation, but also by ionizing radiation. The mechanism of this phenomenon, which is finding extremely wide application (scintillation counters), is still unexplained. In this case, we evidently are not dealing with either direct excitation or ionization of the centers of luminescence.[32] Basically, exposure to hard radiation produces elementary excitation of the host substance, luminescence being excited in a particularly effective manner by the generation of electrons and holes in the crystal. Experiments have shown[21] that at concentrations of thallium in KI-Tl greatly exceeding the concentration of residual crystal defects, each "zone-zone" phototransition leads to luminescence of the activator ion practically without quantum loss (loss less than 20 percent). At these activator concentrations, the principal additional losses suffered upon stimulation by ionizing radiation take place during the early stages of the process, before the formation of slow electrons and holes. If one takes the yield of γ-scintillation of KI-Tl to be 10 percent, then from our data it follows that for each creation of an "electron-hole" pair in the KI crystal by γ-rays, the energy expended exceeds by two or three times the width of the forbidden energy zone. The nature of these losses, which are characteristic of excitation by hard radiation, requires special investigation.

In conclusion, we note that the mechanism of recombination luminescence of activated alkali halide crystals is extremely complicated. To investigate it, it is necessary to study the existence and active role in the production of luminescence of electrons, holes, excitons, and sensitization processes.

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THE LUMINESCENCE PROPERTIES OF SELENIUM-ACTIVATED ZINC OXIDE

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Data on the luminescence properties of selenium-activated zinc oxide are presented. It is shown that the introduction of selenium into zinc oxide causes the appearance in the cathodoluminescence spectrum of a specific band with λ_{max} near 610 mμ. The maximum strength of this band is observed in the two-band luminors containing 0.2 percent Se and having a band due to a stoichiometric excess of zinc, in addition to the selenium band.

Zinc oxide-base luminors have great practical value, since they make it possible, using cathodic excitation, to obtain broad emission bands in the visible region of the spectrum (from 440 to 650 mμ with a maximum at 505 mμ) accompanied by very little persistent afterglow.[1-3]

The theories about the nature of the luminescence of zinc oxide are somewhat controversial;[4-10] however, most authors regard this luminescence as being caused by the presence of a stoichiometric excess of zinc, created in the process of synthesizing the luminor. This process, as is well known, consists either in the combustion of zinc sulfide or metallic zinc in air or oxygen, or in the partial reduction of luminescence grade zinc oxide by hydrogen, carbon monoxide, or carbon.

The luminescence properties of zinc oxide can vary, within certain limits, depending on the conditions of formation of the luminor. Thus, Leverenz has shown[11, 12] that pure zinc oxide obtained by the combustion of metallic zinc in oxygen, under cathodic excitation, has a narrow emission band with a maximum near 385 mμ. Heating (1000°C) in a reducing atmosphere, on the other hand, gives a luminor having an emission band in the visible region of the spectrum (λ_{max} = 505 mμ). According to other authors,[4, 5, 9, 13] zinc oxide with an orange luminescence (λ_{max} 590-630 mμ) can be obtained in certain cases. It has also been reported that cathodically excited orange luminescence is obtained in zinc oxide prepared by the burning of sulfide-selenides of zinc in air.[14, 15]

These observations appeared to justify a more detailed investigation of the possibility of obtaining effective cathodo-luminors with orange luminescence by activating zinc oxide with selenium.

EXPERIMENTAL METHOD

Zinc oxide was prepared by air-ignition of luminescence grade ZnS produced by the "Krasnii Khimik" factory. This material contained the following amounts of heavy metal impurities (in percent): Fe—3×10^{-5}, Cu—5×10^{-6}, Ni and Co—1×10^{-5}. The ignition was carried out in a small open shallow quartz cup placed in the chamber of a globar furnace, with periodic stirring of the powder with a quartz spatula. Selenium was introduced into the charge either in the form of a purified solution of selenious acid (containing less than 3×10^{-5} percent of heavy metal impurities), or in the form of elemental Se ("semiconductor grade"), or luminescence-pure ZnSe, precipitated from a solution of $ZnSO_4$ by passing hydrogen selenide through it.

Measurement of the luminescence properties of the luminors was conducted in a demountable cathode-ray tube, using a scanning beam for excitation. The spectral characteristics of the luminors were measured in an apparatus consisting of a UM-2 universal monochromator, with a FEU-17 photomultiplier connected to its output combined with a GZS-47 mirror galvanometer. Persistence of afterglow was measured by an oscillographic method.[16] Conditions of excitation: V_a = 9kv, I_a = 1 μa/cm². As a comparison standard a sample of the commercial luminor K-56 (ZnO-Zn) was used.

SELECTION OF OPTIMUM CONDITIONS FOR PREPARING THE LUMINOR

In preliminary experiments it was shown that if the oxidation of the mixture of ZnS and selenium compounds (SeO_2 or Se) proceeded without the preliminary formation of zinc sulfide-selenide, then very little selenium (< 0.01 percent) remained in the final product, and the luminescent properties of such a luminor were not distinguishable from the usual zinc oxide obtained without the admixture of selenium. It was also shown that the optimum temperature for heating the first charge was 800° (length of heating 30 min). The most favorable temperature for the air-ignition of the selenide formed in this process was about 750-800°, and the length of heating

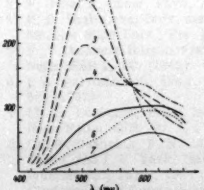

Fig. 1

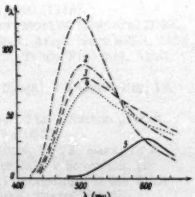

Fig. 2

Fig. 1. Spectral energy distribution curves of the emission spectra of ZnO luminors activated by selenium introduced in the form of SeO_2 (with flux). Curve 1—ZnO-Zn standard; curves 2-7—samples from charges containing 5, 10, 15, 30, 40, and 50 percent SeO_2, respectively.

Fig. 2—Spectral energy distribution curves of the emission spectra of samples activated by elementary selenium (without flux). Curve 1—ZnO-Zn standard; curves 2-4—samples from charges containing 5, 12, and 15 percent Se, respectively; curve 5—ZnO-Se luminor obtained by the combustion of ZnSe.

for batches of the order of 20-25 gm was 1.5 hr (with periodic stirring of the charge).

The results of this study are presented in Figs. 1 and 2 and in Tables 1 and 2.

As is seen from the data presented, the properties of the luminors are almost independent of the form in which the Se was introduced into the charge, but are determined by the quantity of the latter remaining in the luminor and by the conditions of formation of the sample. The introduction of a flux had a particularly marked effect. As a flux we used LiCl, it having been shown that its use increases the degree of penetration of selenium into the ZnO lattice (see the data in Table 1). By means of a careful x-ray investigation using an ionization apparatus, Yu. D. Kondrashev has shown that the introduction of Se does not cause any noticeable change in the lattice parameters of ZnO.

Table 1. Results of Experiments on the Synthesis of the Luminor ZnO-Se from a ZnS + H_2SeO_3 Charge (Temperature of Sulfide-Selenide Formation 800°)

Run no.	Composition of initial charge (wt %)			Se content of luminor by analysis (wt. %)	Temperature of oxidation of sulfide-selenide (°C)	Relative emission brightness (% of standard)	λ_{max} under cathodic excitation (mμ)	Color of luminescence under 365 mμ excitation
	ZnS	SeO_2	LiCl					
1	95	5	—	—	800	78.5	500	green
2	90	10	—	0.07	800	67.0	500	green
3	85	15	—	0.10	800	43.0	510	yellow-green
4	80	20	—	—	800	37.0	500—530	yellow
5	70	30	—	—	800	31.0	—	orange-yellow
6	60	40	—	0.3	800	29.2	600—620	orange
7	50	50	—	0.4	800	27.2	600—620	orange
8	85	15	2	0.2	800	61.0	510—530, 600	yellow
9	85	15	2	—	700	39.4	510	yellow-green
10	85	15	2	—	600	16.0	510	green
11	85	15	2	—	900	45.0	510	green
12	95	5	2	—	800	71.0	500	green
13	90	10	2	0.14	800	62.5	500	green
14	70	30	2	0.3	800	40.0	600—620	yellow-orange
15	60	40	2	0.35	800	29.2	600—620	orange
16	50	50	2	0.4	800	14.8	600—620	orange

Table 1 presents the results of experiments on the production of the luminor ZnO-Se in a charge of ZnS + H_2SeO_3 both without fluxes and also with the addition of LiCl (at a concentration of 2 weight percent, which seemed to be the optimum). Table 2 gives data for charges consisting of ZnS + Se without the use of a flux. Special experiments showed that the use of a flux does not give favorable results with a charge of ZnS + Se.

Table 2. Results of Experiments on the Synthesis of the Luminor ZnO-Se from a Charge of ZnS Mixed with Elementary Selenium (Temperature of Formation of Sulfide-Selenide 800° for 30 min, Temperature of its Oxidation 800° for 1.5 hr)

Run no.	Composition of initial charge (wt %)		Selenium content of luminor by analysis (wt.%)	Relative emission intensity under cathodic excitation (% of standard)	Color of luminescence under 365 mμ excitation
	ZnS	Se			
17	95	5	0.07	91.5	yellow-green
18	90	10	0.14	88.5	yellow
19	88	12	—	88.0	yellow
20	85	15	0.20	75.0	yellow

The results also show that upon increasing the content of SeO_2 and Se in the initial charge the intensity of the green band decreases; simultaneously the intensity of the band with maximum at 610 mμ increases. With 40 percent SeO_2 (without use of flux) the green band with its maximum at 505 mμ disappears completely, and only the band with its maximum at 600-620 mμ remains.

As already mentioned, the introduction of LiCl into the charge along with SeO_2 enhances the uptake of selenium by the ZnO lattice, resulting in a shift of the emission spectrum toward the red. The maximum intensity of emission in the orange band is observed in the two-band luminor obtained from a charge containing 15 percent SeO_2. This luminor also has the optimum intensity of total emission. Its selenium content is 0.2 percent (based on analysis). As is seen from Fig. 1, emission in the orange band is markedly decreased as the Se content of the luminor is increased further.

A picture which is similar, but not quite so clear-cut, can also be seen in luminors synthesized with additions of elementary Se. However, it is not possible to obtain a luminor containing more than 0.2 percent Se by adding elemental Se to the charge, because of the volatility of the selenium. As a result of experiments on a charge consisting of 88 percent ZnS and 12 percent Se, a luminor was obtained having a total intensity equal to 88 percent of that of the commercial sample of luminor K-56, along with a simultaneous increase in the intensity of luminescence in the orange-red region of the spectrum (Fig. 2).

CHARACTERISTICS OF THE LUMINESCENCE PROPERTIES OF SELENIUM-ACTIVATED ZINC OXIDE

The data presented leave no doubt that upon activation of ZnO by Se a specific emission band with λ_{max} = 600-610 mμ appears in the luminescence spectrum. At low selenium concentrations (up to 0.3 percent) it appears together with the band corresponding to superstoichiometric zinc. The two-band luminor so obtained has a persistence of afterglow in the region of the green band of the order of 3×10^{-4} sec. The band belonging to selenium has a persistence of afterglow an order of magnitude greater than the zinc band.

With increasing selenium concentration, as can be seen from the data in Table 1 and the curves in Fig. 1, concentration quenching of the corresponding band is observed. Hence the luminor ZnO-Se, not having a band due to superstoichiometric zinc, has a relatively small intensity (about 30 percent of the standard). The optimum value of intensity with cathodic excitation is obtained from the two-band luminor ZnO-Zn · ZnO-Se containing about 0.2 percent Se. This luminor has an intensity about 90 percent of the standard, but has a high percentage of its emission in the orange-red region of the spectrum. This is confirmed by the data of Table 3, which gives the relative intensity of emission from the luminor ZnO-Zn · ZnO-Se at various wavelengths in comparison with the corresponding data for the luminor ZnO-Zn.

Table 3. Dependence of the Relative Strength of Luminescence of Selenium-Activated Zinc Oxide for Various Wavelengths in Comparison with the Luminor ZnO-Zn (Cathodic Excitation: V_a = 9 kv; $I_a = \mu a/cm^2$)

Concentration of selenium in luminor (wt. %)	Concentration of sulfur in luminor* (wt. %)	Relative intensity (in % of standard) for various wavelengths (in mμ)							
		500	520	540	560	580	600	620	640
0.1	0.34	118	127	143	154	178	180	200	200
0.14	0.27	115	127	150	167	189	200	226	234
0.2	0.26	108	132	154	181	194	218	242	272
0.3	0.2	89	88	110	141	150	200	—	—
0.4	0.4	43	56	70	90	100	137	—	—

*Amount of sulfur remaining in the luminor after ignition of ZnS.

By the air-oxidation of pure zinc selenide (for 30 min at 800°) a luminor is obtained which contains 0.43 percent Se. Its spectral distribution of emission energy is illustrated in Fig. 2 (curve 5).

THE EFFECT OF ADDITIONS OF HEAVY METALS ON THE LUMINESCENCE PROPERTIES OF THE LUMINOR

Data on the effect of additions of heavy metals on the luminescence intensity of the luminor are presented in Table 4. Additions of Cu, Fe, and Ni were made to a charge containing 88 percent ZnS and 12 percent elemental Se.

Table 4. The Effect of Additions of Cu, Fe, and Ni on the Luminescence Intensity of the Luminor ZnO-Se under Cathodic Excitation

Run no.	Addition	Concentration of addition, (weight %)	Relative intensity (%)
1	none	—	91
2	Cu	5×10^{-6}	86.5
3	Cu	1×10^{-4}	77.3
4	Cu	1×10^{-3}	59.3
5	Fe	5×10^{-5}	82.0
6	Fe	1×10^{-4}	80.0
7	Fe	1×10^{-3}	50.7
8	Ni	5×10^{-5}	87.5
9	Ni	1×10^{-4}	86.0
10	Ni	1×10^{-3}	55.0

As is seen from the data, the luminor ZnO-Se is very sensitive to the presence of traces of heavy metals. According to preliminary experiments, additions of Fe and Ni markedly decrease the persistence of afterglow of the luminor, while additions of Cu, on the other hand, increase it.

CONCLUSIONS

1. By the combustion of various sulfide-selenide compositions in air a selenium-activated zinc oxide is obtained which differs in its specific luminescence properties both under photo- and also under cathodo-excitation.

2. The introduction of Se into the ZnO lattice leads to a shift of the spectral energy curve of the luminor to the orange-red region and to the appearance of a selenium band with a maximum at about 610 mμ (under cathodic excitation). The maximum intensity of this band is observed in the two-band luminor having, besides the selenium band, the usual band due to superstoichiometric zinc as well (λ_{max} = 505 mμ).

3. A ZnO-Se luminor not possessing the emission band of superstoichiometric zinc under cathodic excitation contains 0.3-0.4 percent Se and has a strength of the order of 30 percent of the luminor ZnO-Zn.

4. Concentration quenching of the selenium band is observed with further increase of the Se content in ZnO.

5. The persistence of afterglow of the selenium band is about ten times longer than that of the band due to superstoichiometric zinc.

In conclusion, we must express our thanks to F. M. Pekerman for a number of valuable discussions and to O. N. Kazanin for measuring the persistence of the samples.

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EFFECT OF ANNEALING ON THE ABSORPTION SPECTRA AND ELECTRICAL CONDUCTIVITY OF CRYSTALLINE NaCl:Pb AND KCl:Pb PHOSPHORS

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A number of authors have shown the substantial effect of temperature treatment on the luminescence and absorption spectra of KCl and NaCl crystals containing lead and copper.[1-3] In the present study, we compare the effect of prolonged high-temperature annealing on the absorption spectra and the ionic conductivity of lead-activated KCl and NaCl crystals.

The KCl:Pb crystals, which we investigated, were obtained from a melt containing $PbCl_2$ by the Kiropoulos method, and from aqueous solutions in the presence of $PbCl_2$; the NaCl:Pb crystals were grown from the melt only. The absorption spectra were studied by means of an SF-4 spectrophotometer. The activator content was determined polarographically for each individual sample.

We interpret the differences in the absorption spectra of KCl:Pb crystals grown from the melt and from a solution and also of KCl:Pb and NaCl:Pb obtained from the melt, as follows: In the case of NaCl:Cu and NaCl:Ni phosphors, Parfianovich[4] made the supposition that the short wavelength maxima in the absorption spectra are due to impurity ions at "special locations" of the crystal (e.g., at boundaries of mosaic block surfaces in contact). He ascribed the long wavelength maxima to ionic impurities located at the nodes of the crystalline lattice. We may apparently assume in our case, as well, that there is a twofold distribution of impurities in the crystal. We note that the possibility of such a distribution has been discussed in papers by Shamovskii.[5,6]

This assumption is based on the following considerations: First the ratio of intensities of KCl:Pb absorption bands in the 210 and 273 mμ regions differs from that for NaCl:Pb and corresponds to the difference in structural diagrams of the KCl-$PbCl_2$ and NaCl-$PbCl_2$ systems. The first system is characterized by mutual solubility over a rather wide range of concentrations, while the second exhibits very limited solubility. Hence fewer Pb^{++} ions penetrate into the NaCl lattice than into the KCl lattice. This is also consistent with the difference in absorption coefficients at the maxima of the 210 and 273 mμ bands for KCl and NaCl crystals at equal activator concentrations. Secondly, the absorption band of an aqueous $PbCl_2$ solution coincides with the short wavelength maximum of the crystalline KCl:Pb and NaCl:Pb phosphors. This may be correlated with the fact that the lead ions are in about the same energetic conditions in aqueous solutions as on the surfaces of mosaic blocks. The assumption of the twofold distribution of impurities in crystals is furthermore supported by the fact that the intensity of the absorption peak on the short wavelength region of the spectrum is not a single-valued function of impurity concentration, as opposed to the band near 273 mμ. Thus the band in the 273 mμ region should apparently be ascribed to the absorption of light by lead ions located at the lattice nodes of the alkali halide crystals.

This last supposition is also supported by data on the effect of lead on the electrical conductivity of NaCl and KCl crystals. We have shown that Pb^{++} ions have a much greater effect on the electrical conductivity of KCl than on NaCl; i.e., the value of the ionic conductivity is connected with the intensity of the absorption band at 273 mμ. The difference in the absorption coefficients at the maximum of this band for KCl obtained from the melt and from solution is also connected with the difference in the electrical conductivity of these crystals. The absorption coefficient is smaller for crystals obtained from a solution; this is consistent with the lower electrical conductivity shown by these crystals.

These facts indicate that the change in the electrical conductivity of lead-activated alkali halide crystals occurs in correlation with changes in the intensity of the absorption band at 273 mμ. This last can be easily explained if we assume that the band in the 273 mμ region corresponds to the absorption of light by Pb^{++} ions situated at the cationic sites of the crystalline lattice. In this case we are actually dealing with the formation of a solid solution of two salts, of which one has a cation with a charge differing by two from that of the other, the anions being identical. This is accompanied by the formation of vacancies in the cation lattice. Such a system has a higher cation mobility and ionic conductivity.

On the basis of the above, we can expect that prolonged high temperature annealing will cause a redistribution of impurities in the crystal, which will affect both the character of the absorption spectra and the magnitude of the electrical conductivity. Our experiments have shown that the effect of annealing at 600°C reduces to the following:

Figure 1 shows that 5 and 10 hr annealing (and for NaCl:Pb a 20 hr one as well) will cause an increase in the intensity of both absorption bands, accompanied by a simultaneous increase in the electrical conductivity of the crystals. We may explain the observed phenomena as follows: The impurity in an activated crystal may occur in the form of the compound $PbCl_2$. Annealing causes dissociation of the impurity into ions. We may point out that Kuznetsov[7] gives an analogous explanation for the change in certain mechanical properties of rock salt.

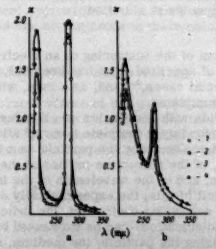

Fig. 1. Effect of annealing on the absorption of light by KCl:Pb (a), and NaCl:Pb (b) crystals. 1—prior to annealing; 2—after annealing for 5 hr; 3—same 10 hr; 4—same 20 hr.

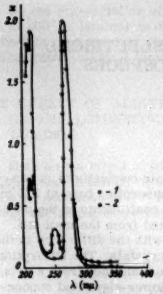

Fig. 2

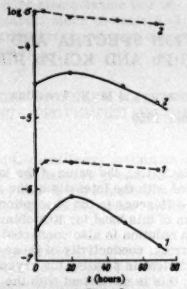

Fig. 3

Fig. 2. Effect of annealing on absorption of light by KCl:Pb crystals. 1—prior to annealing; 2—after annealing for 20 hr.
Fig. 3. Dependence of log σ on annealing time t for KCl:Pb crystals (solid lines) and NaCl:Pb crystals (dashed lines). Annealing temperature (in °C): curve 1—350; curve 2—620.

When KCl:Pb is annealed for 20 hr, the short wavelength absorption band becomes very much weaker, and a third activator band appears in the 250 mμ region (see Fig. 2). This may be connected with the formation of a new chemical compound. (According to Frederix and Scott[8] this may be $PbCl_4$ or $PbCl_2$.) The electrical conductivity of the annealed crystals is not decreased, and the intensity of the long wavelength absorption maximum also remains unchanged. These facts also indicate that electrical conductivity is connected with the absorption band in the 273 mμ region.

Annealing for 50 and 70 hr leads to marked qualitative changes in the absorption spectrum, which becomes identical with that of the $PbCl_2$ crystals. Recrystallization apparently occurs during this length annealing period, i.e., the solid solution separates. There is a decrease in electrical conductivity. (See Fig. 3.)

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ON THE SCATTERING OF LIGHT BY DIELECTRIC ELLIPSOIDS COMPARABLE WITH THE WAVELENGTH

I. A General Expression for the Indicatrix of Scattering of an Ellipsoidal Particle

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The problem of the diffraction of an electromagnetic wave by an anisotropic nonabsorbing ellipsoid is solved in first approximation. Expressions for the indicatrix and coefficient of scattering of particles with refractive indices which are not large are obtained. The dependence of the form of the indicatrix on the dimensions, eccentricity, and orientation of the scattering ellipsoids is clarified.

The problem of the scattering of an electromagnetic wave at solids of specified form has been solved only in a series of special cases,[1-3] and, as a rule, with additional simplifying assumptions.

Among solids with boundaries on all sides only the sphere is described by a complete theory,[4] allowing one to find the field scattered by the particle as a function of its dimensions, of the refractive indices of the particle and the medium, and of the wavelength of the incident light. As a result of this, the experimentally determined quantities—the scattering coefficient, the indicatrix, and the degree of polarization—can be expressed by parameters characterizing the particle, the medium, and the incident wave; i.e., first, the characteristic parameter $\rho = 2\pi a/\lambda$, where a is the particle radius and λ is the wavelength in the external medium, and secondly, the relative refractive index $m = m_1/m_2$, where m_1 and m_2 are the refractive indices of the particle and medium, respectively.

For nonspherical particles there does not exist a similar detailed theory presenting a complete solution of the corresponding limited problem, except for the formal solution obtained by Möglich[5] for the general case of triaxial ellipsoids. There have been examined only different limiting cases and particularly the case of particles, small by comparison with the wavelength, since in this case, as Rayleigh[6] has already shown, it is possible to use the solution of the corresponding electrostatic problem. This method was used by Gans[7] and later developed in the work of Stevenson,[8] who describes the field scattered by the particle in the form of a power series of the characteristic parameter.

The limiting case of completely conducting elongated or compressed ellipsoids of rotation with the symmetry

axis located coincident with the direction of the incident light, was examined by Schulz[9] and Tai.[10] The case of an arbitrary orientation of a conducting ellipsoid, close to the form of a sphere, is examined in reference 11.

For dielectric particles of arbitrary dimensions, but with small refractive index, Shifrin[12] worked out a general method using an integro-differential equation and allowing one to obtain the first and second approximation for the indicatrix and coefficient of scattering of spherical particles. However, in the same author's extension of this method to particles having the form of ellipsoids of rotation[13] an inaccuracy was introduced at the very start, distorting the resulting conclusions.

Therefore, it appeared necessary to us to examine anew the problem of scattering of a light wave by an ellipsoid, at the same time generalizing it for the case of anisotropic ellipsoids, located in a medium with dielectric constant not equal to unity.

In the present work an expression is obtained in the first approximation for the indicatrix of the scattered field, which has the same appearance as the analogous expression obtained by Rayleigh[14] for a sphere with a refractive index which is not large. Thanks to its simplicity, the expression indicated also allows one to determine easily the scattering coefficient. The expressions obtained for the indicatrix and coefficient of scattering in the limiting case of small ellipsoids agree with the analogous expressions of the theory of Gans,[7] and in the other limiting case of ellipsoids of arbitrary dimensions, with form approximating a sphere, they agree with the corresponding formulas of Rayleigh.[14] The present work can be considered as a development and substantial refinement of the Rayleigh-Gans method[15,16] applied to particles having the form of an ellipsoid.

INITIAL APPROXIMATION FOR THE INTERNAL FIELD OF THE PARTICLE

The electric field, determined by the polarization of the particle, is expressed by the Hertz vector π (the polarization potential) appearing in the solution of Maxwell's equations

$$\mathbf{D}(r) = \varepsilon \mathbf{E} = \varepsilon_1 \mathbf{E} + 4\pi \mathbf{P} = \varepsilon_1 \operatorname{rot}\operatorname{rot} \Pi;$$

$$\Pi = \frac{1}{\varepsilon_1} \int \frac{\mathbf{P}(r')}{R} e^{-ik'R} \cdot dv'. \tag{1}$$

Here $\mathbf{P}(r) = (\varepsilon - \varepsilon_1)/4\pi \cdot \mathbf{E}(r)$ is the polarization, differing from zero only at those points where ε differs from the dielectric constant ε_1, i.e., inside the particle; $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ is the distance between the position of the source and the position of observation; $\mathbf{k}'$ is the wave vector of the spherical wave spreading from the point $\mathbf{r}'$.

The external scattered field, according to (1), equals

$$\mathbf{E} = \operatorname{rot}\operatorname{rot} \Pi, \tag{2}$$

since for its calculation knowledge of the distribution of the polarization inside the particle, or what is the same, its internal field, is sufficient. In the zeroth approximation the internal field can be considered equal to the external field

$$\mathbf{E}_i = \mathbf{E}_0 e^{-ikr} \tag{3}$$

and correspondingly, the polarization inside the particle equal to

$$\mathbf{P} = \frac{\varepsilon - \varepsilon_1}{4\pi} \mathbf{E}_0 e^{-ikr}. \tag{4}$$

All of the following approximations can be found by Shifrin's method,[12] starting from the integro-differential equation

$$\mathbf{E}_i(r') = \mathbf{E}_0 e^{-ikr} + \frac{1}{\varepsilon} \operatorname{rot}\operatorname{rot} \int \frac{\varepsilon - \varepsilon_1}{4\pi} \mathbf{E}(r') \cdot \frac{e^{-ik'R}}{R} dv', \tag{5}$$

representing the internal field $\mathbf{E}_i$ in the form of a sum of the external polarizing field (3) and the field (1), determined by the polarization of the volume elements of the particle.

Since, however, even in the case of a sphere the calculation proves to be rather cumbersome, beginning with the second approximation, it is desirable in the calculation of the first approximation for the scattered field to make use of a more accurate value of the internal field. In such a case the more precise first approximation, maintaining a simple form, could actually be considered as a second approximation. An approximate calculation of the field produced by the separate volume elements of the particle, polarized by the external field (3), leads to the following value for the internal field

$$\mathbf{E}_i = \mathbf{E}_{i0} e^{-ikr}, \tag{6}$$

where

$$\mathbf{E}_{i0} = \mathbf{E}_0 + \frac{1}{\varepsilon} \frac{\varepsilon - \varepsilon_1}{4\pi} \operatorname{rot}\operatorname{rot} \left(\mathbf{E}_0 \int \frac{dv'}{R} \right) \tag{7}$$

is the internal field, corresponding to the case of polarization of an ellipsoid in a uniform external field. Indeed, as a result of (5) and (1), we have

$$\mathbf{E}_i = \mathbf{E}_{i0} e^{-ikr} + \frac{1}{\varepsilon} \frac{\varepsilon - \varepsilon_i}{4\pi} \operatorname{rot}\operatorname{rot} \int \frac{\mathbf{E}_0}{R} e^{-ikr'} \cdot e^{-ik'(r-r')} dv' \approx e^{-ikr}$$

$$\times \left\{ \mathbf{E}_0 + \frac{1}{\varepsilon} \frac{\varepsilon - \varepsilon_1}{4\pi} \operatorname{rot}\operatorname{rot} \left(\mathbf{E}_0 \int \frac{e^{i(k-k')(r-r')}}{R} dv' \right) \right\}. \tag{8}$$

Limiting outselves to the first term of the expansion of the exponent, we obtain (6).

Thus, for particles having comparatively small dimensions ($\rho < 1$) and refractive indices, as a first approximation for the internal field one can take the field equal to the internal field of an ellipsoid for the case of polarization in a homogeneous field, but with this having at each point the phase of the external nonhomogeneous field. Correspondingly, the polarization equals

$$\mathbf{P} = \frac{\varepsilon - \varepsilon_1}{4\pi} \mathbf{E}_{i0} e^{-ikr}. \tag{9}$$

In other words, it is assumed here that the nonhomogeneity of the external field manifests itself primarily in the phase of the internal field of the ellipsoid. As far as the direction and amplitude of the internal field are concerned, in first approximation the nonhomogeneity of the external field can be neglected in their calculation.

THE EXTERNAL SCATTERED FIELD

The indicated values of the polarization (4) and (9) must be introduced into formula (2) for the magnitude of the external field, which we first transform with the purpose of obtaining the expression for the scattered field in the wave zone $R = \gg r'$

$$\mathbf{E}(r) = \operatorname{rot}\operatorname{rot} \frac{1}{\varepsilon_1} \int \frac{\mathbf{P}(r')}{R} e^{-ik'R} dv' = \frac{k^2}{\varepsilon_1} \int \left[\frac{\mathbf{R}}{R} \left[\frac{\mathbf{R}}{R} \mathbf{P} \right] \right] e^{-ik'R} dv'$$

$$= \frac{k^2}{\varepsilon_1} \int \mathbf{P}_\perp \frac{e^{-ik'R}}{R} dv'. \tag{10}$$

Here $\mathbf{P}_\perp = [\mathbf{R}_0[\mathbf{R}_0\mathbf{P}]]$ is a vector perpendicular to the direction of scattering and equal in magnitude to the component of the electric moment determining the light in-

tensity scattered in the direction $\mathbf{R}_0$ ($\mathbf{R}_0 = \mathbf{R}/R$, a unit vector). Also, keeping in mind that, as a result of (4) or (9),

$$\mathbf{P}(r) = \mathbf{P}_{0\perp} e^{-ikr},$$

where $\mathbf{P}_{0\perp}$ is the component of the polarization in a homogeneous field, which is constant inside a particle having the form of an ellipsoid[17] (sphere), we obtain for the scattered field of a spherical wave

$$\mathbf{E}(r) = -\frac{k^2}{\varepsilon_1} \mathbf{P}_{0\perp} \frac{e^{-ikr}}{r} I, \tag{11}$$

where

$$I = \int e^{i(\mathbf{k}'-\mathbf{k})\mathbf{r}'} dv'.$$

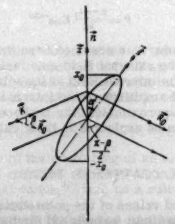
The scattered field thus depends on the magnitude and direction of the polarization vector $\mathbf{P}$ relative to the scattering vector $\mathbf{R}_0$, parallel to $\mathbf{k}'$, and also on the phase relationship between the spherical waves scattered from the separate elements of the particle, since the coefficient I defines the result of interference of these waves. The latter has a maximum value in the case of a small particle, when the phase differences vanish.

The complete phase difference is formed from the initial phase difference in the field of the incident wave ($\mathbf{kr}'$) and the phase difference produced during the scattering in the given direction ($\mathbf{k}'\mathbf{r}'$).

For the calculation of the integral I it is convenient to divide the ellipsoid into layers, for which the vectors $\mathbf{k}$ and $\mathbf{k}'$ will be respectively the vectors of the incident and reflected waves. In this case the phase differences discussed above prove to be equal and the total phase difference consists of (cf. figure) $2kx \sin \beta/2$, so that

$$I = \int_{-x_0}^{x_0} e^{i2kx \sin \frac{\beta}{2}} S(x)\, dx, \tag{12}$$

where β is the scattering angle, x is the layer coordinate, S(x) is the area of the slice, $k = |\mathbf{k}|$ is the wave vector and x_0 and $-x_0$ are the coordinates of the edges of the layer, defined as the distances to the plane tangent to the ellipsoid.



The scattering of light by a dielectric ellipsoid. The axis ξ, forming the angle α with the x axis, has an arbitrary direction relative to the plane containing the vectors $\mathbf{E}$ and $\mathbf{K}$.

It is possible to show that the ends of all perpendiculars erected to the plane tangent to the ellipsoid

$$\frac{x_1^2}{a^2} + \frac{y_1^2}{b^2} + \frac{z_1^2}{b^2} = 1 \tag{13}$$

lie on the surface[18]

$$a^2x_0^2 + b^2y_0^2 + b^2z_0^2 = (x_0^2 + y_0^2 + z_0^2)^2.$$

From this it is possible to show that the x axis, forming the angle α with the symmetry axis of the ellipsoid, intersects this surface at the point

$$x_0 = a\sqrt{1 - \varepsilon^2 \sin^2 \alpha}, \tag{14}$$

where $\varepsilon^2 = a^2 - b^2/a^2$ is the eccentricity of the ellipsoid.

For the determination of the area of the layer we transform the equation of the ellipsoid to the x, y, z, axes by a rotation of the $\mathbf{x}_1$ and $\mathbf{y}_1$ axes about $\mathbf{z}_1$ by the angle α

$$\frac{z^2}{b^2} + \frac{x^2}{B^2} = 1 - \frac{(y - Cx)^2}{\frac{a^2b^2}{B^2}},$$

where $B^2 = b^2 + (a^2 - b^2)\cos^2\alpha$ and

$$C = \frac{b^2 - a^2}{2} \cdot \frac{\sin 2\alpha}{B^2}.$$

Putting $y' = y + Cx$ and taking x to be constant, we obtain the equation of an ellipse formed by the intersection of the ellipsoid with the plane x

$$\frac{z^2}{b^2 \cdot A} + \frac{y'^2}{\frac{a^2b^2}{B^2} \cdot A} = 1,$$

where $A = 1 - (x^2/B^2)$. It follows that

$$s(x) = \pi ab \frac{b}{B} \cdot \left[1 - \frac{x^2}{B^2}\right].$$

Introducing S(x) into (12) and integrating we get

$$I = \pi ab \frac{b}{B} \cdot \int_{-x_0}^{x_0} \left(1 - \frac{x^2}{B^2}\right) e^{-2ikx \sin \frac{\beta}{2}} = vf(q), \tag{15}$$

where $f(q) = (3/q^3)(\sin q - q \cos q)$, and v is the volume of the ellipsoid.

Then the field of the scattered wave, as a result of (11), is equal to

$$\mathbf{E}(r) = -\frac{e^{-ikr}}{r} \frac{k^2}{\varepsilon_1} \mathbf{P}_{0\perp} vf(q),$$

and its intensity (averaged over a period) is

$$I(r) = I_0 \frac{k^4}{\varepsilon_1^2} \frac{P_{0\perp}^2}{E_0^2} v^2 f^2(q), \tag{16}$$

where

$$I_0 = \frac{c}{8\pi} \sqrt{\varepsilon_1} E_0^2 \frac{1}{r^2}.$$

Expression (16) in its form agrees with the formula obtained by Rayleigh for spherical particles with refractive indices close to unity. In our case, however, the parameter q is defined not only by the scattering angle β and the dimensions of the particle, but also by its orientation and eccentricity.

Here the dimension of the particle in the direction normal to the "reflecting" layer proves to to be significant, i.e., from (14)

$$x_0 = a\sqrt{1 - \varepsilon^2(1 - \alpha_1^2)}, \tag{17}$$

where $\alpha_1 = \cos\alpha$, so that

$$q = 2ka \sin\frac{\beta}{2} \sqrt{1 - \varepsilon^2(1 - \alpha_1^2)} = 2\rho \sin\frac{\beta}{2} \sqrt{1 + \sigma\alpha_1^2}.$$

Here $\rho = kb = 2\pi b/\lambda$ and $\sigma = \varepsilon^2/1 - \varepsilon^2$.

We also note that in the case of an ellipsoid the polarization vector in general is not parallel to the electric vector of the incident wave and, accordingly, $\mathbf{P}_{0\perp}$ does not lie in the same plane as $\mathbf{E}_0$ and $\mathbf{R}_0$, so that the

scattered light is depolarized even for a scattering angle $\beta = \pi/2$.

Examining the expression for the indicatrix it is easy to convince oneself that it reduces to the formula of Gans in the case of small ellipsoids ($f(q) \to 1$) and into the Rayleigh formula in the case of ellipsoids approximating the form of a sphere ($\varepsilon = 0$). From (16) the indicatrix depends on the dimensions, form, and orientation of the ellipsoid through the parameters $P_{0\perp}$ and q, where $P_{0\perp}$ is defined by the polarization of the ellipsoid and q by the number of waves contained in the limits of the dimensions of the particle in the direction normal to the "reflecting" layers.

The indicatrices, characterizing the discussed dependences, are given in the second part of the article where the formula for the scattering coefficient is given.

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COMPARISON OF THE ACTIVATION ENERGY FOR THE REORIENTATION OF MOLECULES WITH THE ACTIVATION ENERGY OF VISCOUS FLOW

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Activation energies for reorientation were calculated by the broadening of Raman spectrum lines; these energies were compared with the activation energies for viscous flow. In the majority of cases it was found that $U_{or.} = U_{visc.}$; in the remaining cases $U_{or.} < U_{visc.}$. All of this is connected with the form of the molecules and the nature of intermolecular forces.

In previous papers[1, 2] orientation relaxation times were determined for a number of liquids by the broadening of Raman lines between 20 and 200°C. These measurements showed that the decrease in relaxation time with increasing temperatures obeys a simple exponential law

$$\tau = \tau_0 e^{\frac{U_{or.}}{RT}}, \qquad (1)$$

so that the points lie quite close to straight lines in log τ versus 1/T coordinates. The activation energies for reorientation of molecules, $U_{or.}$, are easily determined from the slopes of these straight lines.

It is interesting to compare these values with the activation energies for diffusion and viscous flow, since in all three cases we are dealing with analogous molecular processes and an almost identical dependence of the corresponding quantities on the temperature. Since the necessary data on diffusion are not available, we shall limit ourselves to a comparison with viscosity.

First, we shall note once more that the values of relaxation times obtained by out method agree quite well, in most cases, with the dipole relaxation times obtained from measurements of dielectric losses. Table 1 shows that the same can be said with regard to the activation energy for reorientation. In all cases in which experimental data are available for both methods, the same, or at least comparable figures were obtained. The discrepancies noted should be ascribed, apparently, to errors in measurements. It seems to us that our figures are more accurate, since they were obtained from measurements over a very wide temperature range, while the temperature range was only 40 or 50° in the experiments on dielectric losses. This is also indicated by the considerable amount of disagreement among the values of the activation energy of dipole relaxation found by different authors.

Table 1. Activation Energy for Reorientation of Molecules Determined by Measurements of Dielectric Losses and by Broadening of Raman Lines

Liquid	Activation energy (in kcal/mole)	
	By dielectric losses	By broadening of Raman lines
Pyridine	2.2 [5]	1.75
Toluene	1.9 [6]	1.70
	2.1 [7]	
Ethylbenzene	2.4 [7]	1.65
Chlorobenzene	2.3 [6]	2.1
Bromobenzene	2.5 [6]	2.3
o-Xylene	2.1 [7]	2.3
m-Xylene	2.3 [7]	2.2
Acetophenone	2.3 [6]	2.9
Benzophenone	4.5 [6]	3.9

Study of the broadening of Raman lines also makes it possible to determine the time of orientation relaxa-

tion and the corresponding activation energy. Comparison of our data with the data of Rezaev[3] and Rakov[4] obtained by the Raman method, also shows satisfactory agreement. Table 2 gives a list of all the liquids for which measurements of the broadening of Raman lines and viscosity are available over a sufficiently wide temperature range. We see that for most of the substances there is surprisingly good agreement between the two sets of figures. We have placed equality signs at all places where the two figures do not differ by more than 10%; that is, where the difference cannot possibly be greater than the error of measurement (the error in determining $U_{or.}$ is approximately 10-15%, while the values of $U_{visc.}$ are determined with an accuracy of 5-8%). In all the remaining cases, $U_{or.} < U_{visc.}$. The presence of this equality sign means that the height of the potential barrier for reorientation of molecules is not less than the height of the barrier for their displacement. However, since the displacement of a molecule is obviously always accompanied by a change in orientation, one can state that in the cases investigated, the reorientation of molecules occurs chiefly as a result of their displacement and, consequently, the speed of the rotational Brownian movement of molecules is determined by the rate of diffusion.

Table 2. Activation Energy for Reorientation and Viscous Flow (in kcal/mole)

Liquid	$U_{or.}$	$U_{visc.}$
Carbon disulfide	1.30 =	1.35
Benzene	1.35 <	2.5
Pyridine	1.75 <	2.5
Toluene	1.70 <	2.2
Ethylbenzene	1.65 <	2.2
o-Xylene	2.3 =	2.3
m-Xylene	2.2 =	2.1
p-Xylene	2.3 =	2.1
Fluorobenzene	2.2 =	2.0
Chlorobenzene	2.1 =	2.2
Bromobenzene	2.3 =	2.2
Iodobenzene	2.4 =	2.4
Anisole	2.6 =	2.5
Acetophenone	2.9 =	3.0
Naphthalene	2.9 =	2.9
Quinoline	2.7 =	3.0
Benzonitrile	3.0 =	2.9
Aniline	3.0 <	3.5 (5.7)
Phenol	3.7 <	3.9 (6.5)
Benzophenone	3.9 <	3.5 (6.4)

For benzene, pyridine, toluene, and ethylbenzene molecules, the height of the potential barrier for reorientation is noticeably lower than the barrier for displacement, $U_{or.} < U_{visc.}$. In these cases, the reorientation of molecules can also take place, apparently, without translational displacement. Here it is no longer possible to state that the speed of reorientation is determined by the rate of diffusion. This group includes the least elongated molecules, which differ little from the spherical form. Such molecules possess increased rotational mobility, since the more closely their shape approaches the spherical and the less their anisotropy, the less the hindrance to Brownian rotation.

Three liquids listed at the end of Table 2 (aniline, phenol, and benzophenone) possess the following peculiarity: in these liquids the log viscosity versus 1/T plot is not a straight line, as in the other cases, but bends upward in the 60-80°C region. It is possible to approximate this curve by two straight lines, one of which represents the dependence of the viscosity on the temperature for temperatures up to 70°C and the other, above this temperature. According to this, we obtain two values of the activation energy for these substances—a smaller one for temperatures above 70° and a larger one for temperatures below 70°. The second of these values is enclosed in brackets in Table 2.

This behavior of the viscosity of aniline, phenol, and benzophenone should be ascribed to the peculiarities in the realization of the intermolecular hydrogen bond. The curves for relaxation times do not show such peculiarities. On comparing $U_{or.}$ with $U_{visc.}$ for the last three liquid, after making the preceding comments, we see that $U_{or.} < U_{visc.}$ for temperatures below 70°, while $U_{or.} = U_{visc.}$ for higher temperatures, as in the case of most of the preceding liquids.

The occurrence of a discrepancy between $U_{or.}$ and $U_{visc.}$ in aniline, phenol, and benzophenone below 70°C can be explained by the fact that when liquids are cooled, associated complexed or chains begin to form. These structures strongly affect viscosity, but have little effect on the speed of the rotational Brownian movement.

The data presented here show that broadening of Raman lines in liquids is closely connected with such phenomena as viscosity and diffusion. The joint study of these phenomena may therefore turn out to be very fruitful.

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NEW RECURSION FORMULAS IN THE THEORY OF MULTILAYER OPTICAL COATINGS

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New recursion formulas for the calculation of multilayer optical coatings are obtained. The Vlasov formulas are presented in the most simple form. It is shown that the results obtained can be used successfully in the calculation of absorbing layers in theory and practice.

INTRODUCTION

The appearance of the recursion formulas of Vlasov may be considered as the beginning of the development of multilayer optical coating theory.[1] In spite of the fact that since that time the theory has advanced considerably, these formulas have remained important. They are widely used in theoretical investigations as well as in practical computations. A combination of the Vlasov method with other methods is usually the most fruitful.

In this work we shall obtain new recursion formulas, outwardly somewhat similar to the Vlasov formulas; however, in essence different from them. It seems probable that in certain cases application of the new formulas may prove to be more convenient than the use of other methods. Moreover, it will be shown how some of the Vlasov formulas can be substantially simplified.

We shall make use of the following notation: N is the number of layers; $n_1, n_2, \ldots n_N$ are the indices of refraction of the layers (the numbers increase in the direction of light propagation); n_0 is the index of refraction of the original medium from which light is incident on the coating; $n_{N+1} = n$ is the index of refraction of the final medium (substrate). Normal incidence will be taken for simplicity, although all conclusions, with the appropriate modifications, are applicable also in the case of oblique incidence (see end of article). Further, let k denote the wave number in vacuum, h_m the thickness of the m-th layer, and

$$a_m = kn_m h_m. \tag{1}$$

Finally, let us take

$$u_m = \frac{1}{2}\ln\frac{n}{n_m}, \quad m = 0, 1, \ldots N. \tag{2}$$

This notation corresponds with that taken in reference 2. The indices of refraction of the layers and the bounding media can be complex, i.e., the corresponding substances are absorbing. We shall limit ourselves here to the case of isotropic substances.

THE VLASOV FORMULAS

We recall first of all the Vlasov formulas. We shall write them in a form somewhat different from usual, namely, by introducing the notation

$$a = \frac{r}{d}, \quad b = \frac{1}{d}, \tag{3}$$

where r and d are the amplitude reflection and transmission coefficients. The energetic coefficients of reflection R, transmission D, and absorption A (in those cases in which this quantity has meaning)* are expressed in terms of a and b in the following way:

$$R = \left|\frac{a}{b}\right|^2, \quad D = \frac{1}{|b|^2}, \quad A = \frac{|b|^2 - |a|^2 - 1}{|b|^2}. \tag{4}$$

We shall use the notation of (3) throughout this article. The Vlasov formulas have a threefold form.

1) In the most general case

$$\left.\begin{aligned} a &= a_1 b_2 e^{iz_m} + a_2 \frac{1 - a_1 a_1}{b_1} e^{-iz_m}, \\ b &= b_1 b_2 e^{iz_m} - a_2 a_1' e^{-iz_m}. \end{aligned}\right\} \tag{5}$$

Here m is the index of an arbitrarily chosen layer in the coating which divides the latter into two subcoatings —that turned toward the initial medium (first) and that turned toward the final medium (second). The quantities a_1, b_1, and a_2, b_2 refer, respectively, to the first and second subcoatings, while the substance of the m-th layer must be considered as one of the bounding media for the subcoatings—the final medium for the first subcoating and the initial one for the second. The parameter a_1' refers also to the first subcoating but for the case of light propagated in the opposite direction (i.e., from the m-th layer). The quantities a and b refer to the entire coating.

2) If m = 1, i.e., the first subcoating degenerates into a simple boundary separating the media, then $a_1' = -a_1$ and $b_1^2 - a_1^2 = 1$, as a consequence of which

$$\left.\begin{aligned} a &= a_1 b_2 e^{iz_m} + a_2 b_1 e^{-iz_m}, \\ b &= b_1 b_2 e^{iz_m} + a_1 a_2 e^{-iz_m}. \end{aligned}\right\} \tag{6}$$

3) If the first subcoating, the initial medium, and the m-th layer are transparent (i.e., there is no absorption in them), then $a_1' = -a_1^*$ and $b_1 b_1^* - a_1 a_1^* = 1$. In this case

$$\left.\begin{aligned} a &= a_1 b_2 e^{iz_m} + a_2 b_1^* e^{-iz_m}, \\ b &= b_1 b_2 e^{iz_m} + a_2 a_1^* e^{-iz_m}. \end{aligned}\right\} \tag{7}$$

It must be noted that Eqs. (6) are not contained in Eqs. (7) as a trivial special case since they are true also in the case that the initial medium or the first layer are absorbing (a_1 and b_1 are complex quantities).

Since all formulas of this section are written in notation somewhat different from the usual, we refer the reader to reference 4, where their detailed derivation is given together with literature citations.

NEW RECURSION FORMULAS

The Vlasov formulas reduce the calculation of the coefficients a and b for a given coating to the calculation of the same coefficients for a coating with a smaller number of layers. In this sense our new formulas are analogous to the Vlasov formulas. We present them in two versions.

First version

$$\left.\begin{aligned} a &= a_1 \cos z_m - i a_{11} \sin z_m, \\ b &= b_1 \cos z_m + i b_{11} \sin z_m. \end{aligned}\right\} \tag{8}$$

*This may not be so in those cases in which the indices of refraction of the bounding media take on complex values.

In these formulas a_I, b_I and a_{II}, b_{II} refer to two (N – 1)-layer coatings, which differ from the given N-layer coating in the following properties: coating I in the absence of the m-th layer; coating II in the absence of the m-th layer and in a change in magnitude of the indices of refraction of the initial medium and all layers preceding the m-th according to the formula

$$n_r \to \frac{n_m^2}{n_r}, \qquad r = 0, 1, \ldots m-1. \tag{9}$$

In other respects these two coatings have the same parameters as the given coating.

Second version

$$\left.\begin{aligned} a &= a_I \cos \alpha_m + i a_{III} \sin \alpha_m, \\ b &= b_I \cos \alpha_m + i b_{III} \sin \alpha_m. \end{aligned}\right\} \tag{10}$$

Here a_I and b_I have the same values as in the first version, but a_{III} and b_{III} refer to a coating which differs from the given one in the absence of the m-th layer and in a change in magnitude of the indices of refraction of the final medium and all layers following the m-th according to the formula

$$n_r \to \frac{n_m^2}{n_r}, \quad r = m+1, \; m+2, \ldots N+1. \tag{11}$$

In other respects coating III has the same parameters as the given coating.

Formulas (8) and (10) are derived directly from the following general formula:*

*The derivation of this formula is given by the author in reference 2, although the formula itself is not written down there in the form in which it is presented here (see reference 3). It should also be noted that the reservation in reference 2 concerning applicability of this formula exclusively to nonabsorbing coatings is unnecessary, since actually the formula does not assume the absence of absorption (see, in this connection, references 3 and 4).

$$F = \sum i \sin a_{k_1} i \sin a_{k_2} \ldots i \sin a_{k_s} \cos a_{l_1} \cos a_{l_2} \ldots \tag{12}$$

$$\ldots \cos a_{l_{N-s}} \overset{(-)^s}{G} (2u_{k_s} - 2u_{k_{s-1}} + - \ldots - (-1)^s 2u_{k_1} + (-1)^s u_0),$$

where $k_1 < k_2 < \ldots < k_s$ and the summation is taken over all ways of distributing the indices 1, 2, ... N in the two groups $k_1, k_2, \ldots k_s$ and $l_1, l_2, \ldots l_{N-s}$ ($s = 0, 1, \ldots N$). It is easy to see that the number of these ways is equal to 2^N. Further,

$$G(u) = \begin{pmatrix} \cosh u & \cosh u \\ \sinh u & \sinh u \end{pmatrix}, \quad \overset{*}{G}(u) = \begin{pmatrix} -\cosh u & \cosh u \\ -\sinh u & \sinh u \end{pmatrix}, \tag{13}$$

where $\overset{*}{G} \equiv G$, and

$$F = \begin{pmatrix} \dfrac{1 - aa'}{b} & a' \\ -a & b \end{pmatrix}. \tag{14}$$

In order to obtain Eqs. (8) and (10) from Eq. (12) we collect separately all terms of the sum in Eq. (12) which contain $\cos \alpha_m$ and $i \sin \alpha_m$. Then we can write

$$F = F_I \cos \alpha_m + i F_{II} \cos \alpha_m. \tag{15}$$

Since the arguments of the matrices G and $\overset{*}{G}$ of expression (12) do not depend on the index m in terms containing $\cos \alpha_m$, it is clear that the matrix F_I describes, according to Eq. (14), a coating without the m-th layer. This indicates that

$$F_I = \begin{pmatrix} \dfrac{1 - a_I a_I'}{b_I} & a_I' \\ -a_I & b_I \end{pmatrix}. \tag{16}$$

Let us consider, now, the matrix F_{II}. In each of their terms the matrices G or $\overset{*}{G}$ contain $2u_m$ in the argument. Let $k_j = m$ in any term. Then

$$\begin{aligned} &\overset{(-)^s}{G}(2u_{k_s} - 2u_{k_{s-1}} + - \ldots - (-1)^{s-j} 2u_{k_{j-1}} + (-1)^{s-j} 2u_m \\ &\quad - (-1)^{s-j} 2u_{k_{j+1}} + - \ldots - (-1)^s 2u_{k_1} + (-1)^s u_0) \\ &= \overset{(-)^{s'+1}}{G}(2u_{k_s} - 2u_{k_{s-1}} + - \ldots - (-1)^{s-j} 2u_{k_{j-1}} \\ &\quad + (-1)^{s-j}(4u_m - 2u_{k_{j+1}}) - (-1)^{s-j}(4u_m - 2u_{k_{j+2}}) + - \ldots \\ &\quad \ldots - (-1)^{s'}(4u_m - 2u_{k_1}) + (-1)^{s'}(2u_m - u_0)), \end{aligned} \tag{17}$$

where $s' = s - 1$. In the transformed argument the index m drops out of the sequence of indices $k_s, k_{s-1}, \ldots k_1$, and terms with indices less than m undergo the substitution $(u_r - 2u_m - u_r)$, which, according to Eq. (2), corresponds exactly to the substitution $n_r - n_m^2/n_r$ (see formula (9)). Thus the matrix F_{II} described a coating which differs from the given one in the absence of the m-th layer and in the substitution of index of refraction according to formula (9). Moreover, it is necessary also to take into account here the substitution $G \equiv \overset{*}{G}$, which follows from the substituion $s \to s' + 1$ in (17). Consequently, considering also (13), we find

$$F_{II} = \begin{pmatrix} -\dfrac{1 - a_{II} a_{II}'}{b_{II}} & a_{II}' \\ a_{II} & b_{II} \end{pmatrix}. \tag{18}$$

Combining Eqs. (14), (15), (16), and (18), we get

$$\begin{pmatrix} \dfrac{1 - aa'}{b} & a' \\ -a & b \end{pmatrix} = \begin{pmatrix} \dfrac{1 - a_I a_I'}{b_I} & a_I' \\ -a_I & b_I \end{pmatrix} \cos \alpha_m + i \begin{pmatrix} -\dfrac{1 - a_{II} a_{II}'}{b_{II}} & a_{II}' \\ a_{II} & b_{II} \end{pmatrix} \sin \alpha_m. \tag{19}$$

from which Eqs. (8) follow immediately. As for Eqs. (10), they are obtained if light incident from the opposite side is considered to be incident in the forward direction. In fact, from (19) follows

$$a' = a_I' \cos \alpha_m + i a_{II}' \sin \alpha_m. \tag{a}$$

Dropping the primes in accordance with the above and considering that the change in direction corresponds to a transition from formula (9) to formula (11), we find

$$a = a_I \cos \alpha_m + i a_{III} \sin \alpha_m. \tag{b}$$

It is easy to see that this is the first of Eqs. (10). The second is obtained directly from the fact that for any coating

$$b' = b. \tag{20}$$

Thus the correctness of our Eqs. (8) and (10) is shown. As already mentioned above, they do not replace other formulas in the theory of multilayer coatings, such as the Vlasov formulas, but supplement them. In certain cases they may prove to be preferable to other formulas.

DERIVATION OF CERTAIN NEW RELATIONSHIPS AND SIMPLIFICATION OF THE VLASOV FORMULAS

We begin here with the introduction of the concepts of reverse, conjugate, and reverse-conjugate coatings. A coating is called reverse relative to a given one if the bounding media and layers are distributed in it in the re-

verse order, but all parameters are the same. Quantities which refer to a reverse coating will be denoted by a prime.* A coating is called conjugate relative to a given one if the indices of refraction of the layers and bounding media in them are complex-conjugate quantities, but the thicknesses of the layers and their order are the same. Of course, the conjugate coating is not a real one; however, this is immaterial. Quantities which refer to a conjugate coating will be denoted by the sign ~. Finally, reverse-conjugate coatings are those which are simultaneously reverse and conjugate. We shall denote them by both the prime and the ~-sign.

*The concept of a reverse coating is introduced for convenience. Previously, instead of this, we have considered the light incident on the coating from the opposite side, which serves the same purpose.

We shall now prove two important theorems.

Theorem 1

$$\tilde{a}' = -a^*. \tag{21}$$

For the proof we shall show that this theorem is true for any N-layer coating if it is true for all (N − 1)-layer coatings. By applying the first of Eqs. (10) to a reverse-conjugate coating, we have

$$\tilde{a}' = \tilde{a}'_1 \cos\alpha_m^* + i\tilde{a}'_{II} \sin\alpha_m^* \tag{c}$$

(in the second term a_{III} must be replaced by a_{II} in view of the fact that the order of the media is reversed). Since we are assuming that the theorem is true for all (N − 1)-layer coatings, $\tilde{a}'_1 = -a_1^*$ and $\tilde{a}'_{II} = -a_{II}^*$. Consequently,

$$\tilde{a}' = -a_1^* \cos\alpha_m^* - ia_{II}^* \sin\alpha_m^*. \tag{d}$$

Comparing this expression with the first of Eqs. (8), we see that $\tilde{a}' = -a^*$, i.e., the theorem is also true for an N-layer coating. Thus, the theorem is proved completely, since for any 0-layer coating (i.e., for a simple boundary separating two media) it is obviously true on the strength of the Fresnel equations.

Equation (21) can also be written in the form

$$a' = -\tilde{a}^*. \tag{22}$$

A special case of this theorem is the well-known relationship

$$a' = -a^*, \tag{23}$$

correct for a nonabsorbing coating, which is identical with its conjugate.

Theorem 2

$$b\tilde{b}^* - a\tilde{a}^* = 1. \tag{24}$$

For the proof we turn to Eqs. (12) and (14), and, along the way, we will obtain a second proof of the first theorem. In the transition from a given coating to the conjugate one all quantities α and u, according to (1) and (2), become α^* and u^*. From this it follows that in Eq. (12) all terms of the sum for which s is even transform into complex-conjugate quantities and all terms for which s is odd transform into complex-conjugates and change sign. This means, according to (13), that F_{22} becomes F_{11}^* and vice versa and that F_{12} becomes F_{21}^* and vice versa. Designating by $\tilde{F}$ the matrix F for the conjugate coating, we have on the basis of the above

$$\tilde{F} = \begin{pmatrix} \dfrac{1-a\tilde{a}'}{b} & \tilde{a}' \\ -\tilde{a} & b \end{pmatrix} = \begin{pmatrix} b^* & -a^* \\ a'^* & \dfrac{1-a^*a'^*}{b^*} \end{pmatrix}. \tag{e}$$

From here follows, the first, $a' = -\tilde{a}^*$, which was already proved by a different method, and, secondly, $1 - \tilde{a}\tilde{a}' = \tilde{b}b^*$. Replacing $\tilde{a}'$ by $-a^*$ and changing to the complex-conjugate, we get

$$1 + a\tilde{a}^* = b\tilde{b}^*, \tag{f}$$

which was to be proved.

Now we can write Eq. (14) in a more simple and symmetric form

$$F = \begin{pmatrix} \tilde{b}^* & \tilde{a}^* \\ -a & b \end{pmatrix}, \tag{25}$$

and the Vlasov formulas (5) take the form

$$\left.\begin{aligned} a &= a_1 b_2 e^{i\alpha_m} + a_2 \tilde{b}_1^* e^{-i\alpha_m}, \\ b &= b_1 b_2 e^{i\alpha_m} + a_1^* a_2 e^{-i\alpha_m}. \end{aligned}\right\} \tag{26}$$

Special cases of the Vlasov formulas (see expressions (6) and (7)) follow from these results extremely simply: if the first subcoating is a 0-layer one, then $\tilde{a}_1^* = a_1^*$, $\tilde{b}_1^* = b_1^*$; and if the first subcoating (together with the m-th layer) is transparent, then $\tilde{a}_1^* = a_1^*$, $\tilde{b}_1^* = b_1^*$.

Equations (26) are very convenient in the theory of absorbing coatings. This problem will be considered separately in another article.

Finally, we consider briefly the case of oblique incidence of light. In this case Eqs. (8) and (10) remain in force with, however, the difference that the indices of refraction for coatings denoted above by the indices II and III are expressed not by formulas (9) and (11) but by more complex relationships which include the angle of incidence and whose form depends on the polarization of the incident light. It is not necessary to dwell on this question in detail since it is well-known that the case of oblique incidence can be reduced to the case of normal incidence (see, for example, reference 5), which makes it possible to easily derive the relationships mentioned.

With respect to Eqs. (25) and (26), in the case of oblique incidence the transition to the conjugate coating implies (on the strength of Snell's law) that the angle of incidence and all the angles of refraction must be replaced by complex-conjugate quantities. On this basis Eq. (25) and the simplified Vlasov formulas (26) retain universal applicability, including also the case of total reflection.

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THRESHOLD SENSITIVITY OF RADIATION RECEIVERS

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The relationship of the sensitivity threshold of radiation receivers, as determined by the fluctuations in the effectively absorbed quanta, to the magnitude of the steady background and certain properties of the receiver-amplifier-indicator system is considered.

The threshold sensitivity of radiation receivers, considered independently of their construction, purpose, and principle of action, is usually specified in terms of the smallest amount of radiation which can be detected with a given probability p by means of a single observation with the given receiver. If the time t during which the receiver is irradiated exceeds the time constant τ of the receiver, then what is determined is the threshold power P_0 of the receiver. In the case of a pulse of radiation, for which $t \ll \tau$, the specification of threshold sensitivity is understood in the sense of an energy threshold W_0. For selective receivers the spectral composition of the radiation must be specified or else its power (energy) must be defined relative to the spectral sensitivity of the receiver.

As the threshold criterion in the case of an electrical output indicator, it is customary to take a condition of the form

$$\frac{U_s}{U_n} = m, \tag{1}$$

where U_s is the signal voltage at the output of the system from the detected radiation, U_n is the noise output voltage in the absence of signal, and m is a coefficient determined by the required magnitude of the probability p. The constancy of the magnitude of the ratio of signal to noise as a threshold condition is used even with other types of output indicators.

It is not difficult to convince oneself that in a number of cases criterion (1) gives results which are known to be incorrect. Let us consider the simplest possible system, in which the receiver is irradiated in turn either with background radiation alone or simultaneously with both the background radiation and the radiation that is subject to detection. (A system of this kind is analogous to a compensated system in which one measures the difference in the fluxes on duplicate receivers, one of which is irradiated only by the background radiation and the other of which is irradiated by both the background radiation and the radiation that is subject to detection.) Let this system (receiver, amplifier, and output indicator) be ideal, free from self-generated noise and possessed of sufficient amplification to register each quantum effectively absorbed by the receiver. For such a system with normal distribution of the deviations expression (1) implies the proportionality of the threshold flux to the square root of the background intensity, that is,

$$\frac{c_0 P_0}{\sqrt{c_b P_b}} = m, \tag{2}$$

where P_b is the magnitude of the background flux on which the threshold flux P_0 is detected, c_0 and c_b are constants depending on the spectral composition of the fluxes P_0 and P_b, and also on the spectral and absolute sensitivity of the receiver, and the time constant τ of the system.

In the absence of extraneous irradiation of the receiver ($P_b = 0$), expression (2) leads to an absurd result ($P_0 = 0$), that is, to the conclusion that it would be possible to register indefinitely small irradiations, a conclusion incompatible with the quantum nature of light. For large background intensities formula (2) agrees well with experiment, and an explanation of its apparent incorrectness for small values of P_b should be given.

Relation (2) is based on the assumption that the average number $\overline{N}_0$ of quanta of the threshold flux P_0 effectively absorbed by the receiver and registered by the system in time τ at the threshold is m times as large as the mean square deviation $\sqrt{\overline{N}_b}$ of the corresponding number N_b of quanta of the background flux P_b. That is,

$$\bar{N}_0 = m\sqrt{\overline{N}_b}. \tag{3}$$

It may be readily shown that in the region $\overline{N}_b \gg \overline{N}_0$ this condition actually satisfies the requirement of the constancy of the magnitude of the probability $p(N_0 + N_b > N_b)$. On taking account of the fluctuations not only in the number N_b but also in N_0, the magnitude of the standard deviation $\sigma(\Delta N)$ of the excess of the signal over the background level

$$\Delta N = (N_0 + N_b) - N_b$$

from the average value of the signal N_0 amounts to

$$\sqrt{2\bar{N}_b + \bar{N}_0}.$$

For $\overline{N}_b \gg \overline{N}_0$ we have $\sigma(\Delta N) = \sqrt{2\overline{N}_b}$. Let $m = \sqrt{2}$. Then ΔN will remain positive, that is, the irradiation N_0 will be detected in the presence of the background N_b for all positive deviations ΔN from $\overline{\Delta N}$ (50% of all deviations) and also for negative deviations ΔN which do not exceed the standard deviation (34% of all deviations for the case of the normal curve). Thus, for $\overline{N}_b \gg \overline{N}_0$ condition (2) actually corresponds to a constant probability of detecting the irradiation. (For example, $p = 0.84$ for $m = 2$.)

We should make a remark here concerning the significance of the magnitude of p. If, say, $p = 0.7$, then on the average in 70 out of 100 individual observations the indicated output will be greater for the irradiation undergoing detection plus background radiation falling on the receiver than for irradiation of the receiver by background radiation alone.* The recording of such a signal in 70 cases out of 100 will even serve as an indicator of irradiation above the background level. The larger p is, the smaller is the number of observations needed to detect this irradiation. However, the value of p does not in itself completely reflect the character of the measurements. Actually, $p = 0.5$ does not mean that in 50% of the cases we detect an irradiation equal to twice the background, but rather that there is no such irradiation, that

*What is said here is true not only when applied to two successive readings of an output indicator, but also for measurements using a compensated arrangement.

is, that we have to do with fluctuations in the "pure" background. From this it follows, first, that for a threshold a sufficiently high value of p (for example, p = 0.84, as in the example just considered) must be taken; secondly, that it is desirable that some other parameter be used instead of (or along with) the magnitude of p to characterize the reliability of registration. Many such parameters may be proposed, for example, $q' = (p - 0.5)/0.5 = 2p - 1$ (the increase in the probability of a positive signal during the occurrence of irradiation, relative to the maximum value of this increase), or the quantity of information, expressed as a power of 2, $q'' = \log_2(p/0.5)$.

Both of these parameters are equal to zero in the absence of irradiation above the background level and are equal to unity for p = 1.0.

The replacement of the probability p of obtaining a positive signal for irradiation above the level of the background by a parameter such as q' or q'' is not always necessary. Let us consider, for example, the problem of detecting a bright spot on some given background. Let the probability that the signal corresponding to a doubling of the irradiation falling on the given spot on the receiver surface will be positive be equal to p. Then the magnitude of p will actually be the probability of detecting a doubling of the irradiation, since the probability of a positive (that is, exceeding the value of the signals at all the other points of the field) signal at just the given point is very small without a doubling of the irradiation. (In this case $q' \approx (p - 0)/1 = p$.)

However, in the region of comparatively small background levels condition (3) does not preserve the constancy of the magnitude of $p(N_0 + N_b > N_b)$, and hence it cannot be the correct representation of the dependence of the threshold on the background. For any single observation (that is, for a single comparison of the magnitudes $N_0 + N_b$ and N_b) ΔN will be positive for all positive deviations ΔN and also for deviations ΔN in the negative direction from the average value $\overline{N}_0$, which do not exceed the magnitude of $\overline{N}_0$. The probability $p(N_0 + N_b \geq N_b)$ will consequently be equal to the sum of the probability of a positive deviation ΔN and the probability of a negative deviation not exceeding $\overline{N}_0$ in absolute value, that is

$$p(N_0 + N_b \geq N) = 0.5 + f(n),$$

where

$$n = \frac{\overline{N}_0}{\sigma(\Delta N)} = \frac{\overline{N}_0}{\sqrt{2\overline{N}_b + \overline{N}_0}}.$$

It is clear that for n = const. and p = const., that is, for the threshold condition, we do not have expression (3), but rather the relation

$$\overline{N}_0 = n\sqrt{2\overline{N}_b + \overline{N}_0}. \qquad (4)$$

The dependence of p on n is shown in Table 1.

Table 1

n . .	0.00	0.50	1.0	1.5	2.0
p . .	0.50	0.69	0.84	0.93	0.98
q' . .	0.00	0.38	0.68	0.86	0.96
q'' . .	0.00	0.46	0.75	0.90	0.97

Expression (3) follows from (4) only for the condition $2\overline{N}_b \gg \overline{N}_0$. For small background levels the magnitude of $\overline{N}_0$ cannot be neglected under the square root sign, and we obtain from (4) rather than from (3) the following equation for the threshold number of quanta (for n = 1):

$$\overline{N}_0^2 - \overline{N}_0 - 2\overline{N}_b = 0,$$

whence

$$\overline{N}_0 = \frac{1 + \sqrt{1 + 8\overline{N}_b}}{2} = 0.5 + \sqrt{0.25 + 2\overline{N}_b}. \qquad (5)^*$$

*Equation (4) has also a second, negative root, which we shall not consider at this time.

Expression (5) corresponds to a detection probability p = 0.84. In other words, in the region of large background levels the threshold condition (4) for n = 1 coincides with the generally accepted condition (3) for $m = \sqrt{2}$.

Curves showing the dependence of the number $\overline{N}_0$ of effectively absorbed quanta on the background level $\overline{N}_b$ are given in Fig. 1. These curves were drawn in accordance with formula (3) for m = 1 and $m = \sqrt{2}$ (curves 1 and 2, respectively) and in accordance with formula (5) for n = 1 (curve 3). From the figure it is clearly evident that in the region of weak background intensities it is quite necessary to take account of the fluctuations in the flux which is undergoing detection. Taking account of these fluctuations eliminates the basic disagreement of expression (3) with experiment—unlimited decrease in the threshold with decrease in the background level—and agrees with the experimental fact that in the region of small background intensities the threshold is practically independent of the level of the latter. The last mentioned circumstance is the reason for the inapplicability of criterion (3) in the region of small background levels.

Expression (5), as distinguished from the generally accepted condition (3), does not contradict experiment inasmuch as it correctly describes the general dependence

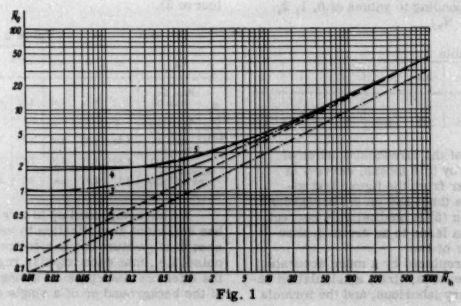

Fig. 1

of the threshold on the background. The question of the validity of the absolute values of the threshold number of quanta as determined by expression (5) should be clarified. In the absence of background ($\overline{N}_b = 0$) the receiver threshold, according to formula (5), must correspond on the average to a single effectively absorbed quantum ($\overline{N}_0 = 1$). It is interesting to note that in the literature[1] for the particular case of absolute threshold ($\overline{N}_b = 0$) the value $\overline{N}_0 = 1$ is also given, but is not obtained as a derivation from relation (5), but by means of considerations relating directly to this particular case. In order to check the last result we use a stricter means of determining the fluctuation threshold than was used in the derivation of formula (5). For a given average value of the intensity of the total irradiation $\overline{N}' = \overline{N}_0 + \overline{N}_b$ the probability that N' will be equal to i is determined by the Poisson formula

$$p(N' = i) = \frac{\overline{N}'^i}{i!} e^{-\overline{N}'}.$$

The probability that for irradiation by the background along N_b will be equal to or greater than i may be calculated with the aid of the Poisson integral function

$$p(N_b \geq i) = Q(i) = \sum_{i=i}^{\infty} \frac{\overline{N}_b^i}{i!} e^{-\overline{N}_b}.$$

Hence the probability that the number N_b of quanta effectively absorbed from the background irradiation will be equal to the corresponding number of quanta $N' = N_0 + N_b$ from the total irradiation or will exceed the latter may be found from the expression

$$p(N_b \geq N_0 + N_b) = \sum_{i=0}^{\infty} \frac{\overline{N}^i}{i!} e^{-\overline{N}'} \sum_{i=i}^{\infty} \frac{\overline{N}_b^i}{i!} e^{-\overline{N}_b},$$

whence the probability of a positive result for a single observation with given N_0 and N_b may be written in the form

$$p(N_0 + N_b > N_b) = 1 - p(N_b \geq N_0 + N_b) = 1 - \sum_{i=0}^{\infty} \frac{\overline{N}^i}{i!} e^{-\overline{N}} \sum_{i=i}^{\infty} \frac{\overline{N}_b^i}{i!} e^{-\overline{N}_b}. \quad (6)$$

If we calculate these values and plot curves showing the dependence of $p(N_0 + N_b > N_b)$ on $\overline{N}_0$ for $\overline{N}_b$ = const., we can find from the graph the threshold $\overline{N}_b$ corresponding to any previously chosen probability, for example, p = 0.84, a value mentioned above. The results of the calculations are presented in Table 2 and in Fig. 2 (curves 1 through 5 corresponding to values of 0, 1, 2, 4, and 10, respectively, for $\overline{N}_b$).

Table 2

$\overline{N}_\Phi$	0	0.1	0.3	0.5	1	2	4	10
$\overline{N}_0$ (for p = 0.84 according to formula (6)	1.84	1.92	2.05	2.22	2.53	3.11	3.88	5.48

From accurate values of the threshold number of quanta which were obtained by this means, curve 4 in Fig. 1 was drawn. It is clear from the figure that although the dependence of the threshold on the background which is given by expression (5) is qualitatively correct, nevertheless this expression leads to an error in absolute value of almost a factor of two.

Equation (5) should be replaced by a more accurate equation for the following reasons: first, a calculation according to formula (6) is very laborious, and the formula

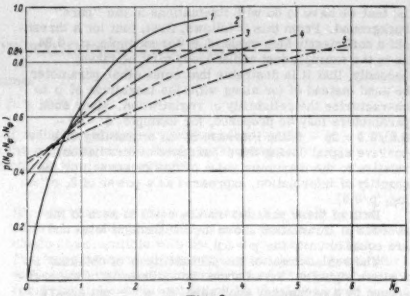

Fig. 2

itself cannot be reduced to analytical form; secondly, it is of interest to explain the origins of the inaccuracy of formula (5) and to remove them while deriving a more accurate relationship.

Formula (5) was obtained from the probability condition as to the fulfillment of the equation $N_0 + N_b = N_b$, that is, the minimum excess of $N_0 + N_b$ over N_b, and not the probability of $N_0 + N_b$ exceeding N_b by at least one quantum, as is the case in the calculations according to formula (6). Hence it would be more correct to determine the threshold for a given value of the probability $p(N_0 + N_b \geq N_b + 1)$. For p = 0.84 this gives $\overline{N}_0 = \sqrt{2\overline{N}_b + \overline{N}_0} + 1$, from which it follows in turn that

$$\overline{N}_0 = \frac{3 + \sqrt{5 + 8\overline{N}_b}}{2} = 1.5 + \sqrt{1.25 + 2\overline{N}_b}. \quad (7)$$

Calculation shows that even though formula (7) is not completely accurate, it gives an error which is only about two thirds as large as that given by formula (5) and which is evidently connected with the departure of the deviation ΔN from the symmetry of the normal law in the region of very small $\overline{N}$. Practically complete agreement with the exact formula (6) is given by the formula

$$\overline{N}_0 = 1 + \sqrt{0.75 + 2\overline{N}_b}, \quad (8)$$

which is obtained from the condition

$$\overline{N}_0 = \sqrt{2\overline{N}_b + \overline{N}_0} + 0.5.$$

These results are illustrated in Table 3 and Fig. 1 (curve 5).

Table 3

$\overline{N}_\Phi$		0	0.1	0.3	0.5	1	2	4	10	100	1000
$\overline{N}_0$ (for p = 0.84)	From formula (5)	1	1.17	1.42	1.62	2.0	2.56	3.36	5.0	14.65	45.25
	Exact value from formula (6)	1.84	1.92	2.05	2.22	2.53	3.11	3.88	5.48	—	—
	From formula (8)	1.86	1.97	2.16	2.32	2.66	3.18	3.96	5.55	15.45	45.7
Error in formula (8) (%)		1.1	2.6	5.4	4.5	5.1	2.2	2.1	1.3	—	—

We have supposed up to now that the system not only has sufficient amplification to register each effectively absorbed quantum but is also free from self-generated noise, i.e., that each impulse registered is the result of the effective absorption of a single quantum of radiation of the background or of a single quantum of the radiation

which is undergoing detection. We now consider a system with sufficient amplification but also with self-generated noise. We limit ourselves to the simplest case, where the only source of noise is the radiation receiver itself. With noise of this type there will be introduced into the system impulses similar to those resulting from the absorption of quanta. Let the average number of such impulses occurring during a time equal to the time constant τ of the system be equal to $\overline{N}_n$. The nature of these noise impulses is immaterial, provided only that their distribution follows the normal (more exactly, the Poisson) law. In this case the total number of impulses from the background and noise will be equal to $\overline{N}_b + \overline{N}_n$, and this sum takes the place of N_b in all the relations introduced above. Hence in the presence of self-generated noise in the receiver, expression (8) for the threshold has the form

$$\overline{N}_0 = 1 + \sqrt{0.75 + 2(\overline{N}_b + \overline{N}_n)}. \qquad (9)$$

A graph of relationship (9) (if the numbers of impulses $\overline{N}_b$ and $\overline{N}_n$ are plotted not on a logarithmic scale, as in Fig. 1, but on a linear scale) does not differ from the analogous graph constructed in accordance with formula (8) for a noise-free receiver and is merely shifted along the abscissa by an amount $\overline{N}_n$.

We now consider a system in which the amplification and sensitivity of the ultimate indicator are insufficient to register impulses produced by the absorption of single quanta, i.e., a system which operates only under the action of groups of l impulses. Without considering the mechanism of such a system (for example, the accumulation of the l impulses, the reading in terms of complete scale divisions on the output measuring device, and so forth), supposing only that the amplification of the system and the sensitivity of the indicator do not fluctuate, that is, that the number l is constant and does not depend on the grouping of the l impulses in time beyond the period τ preceding the instant of reading. Under the assumption of such conditions the threshold condition takes the form

$$\overline{N}_0 - \sqrt{2(\overline{N}_b + \overline{N}_n) + \overline{N}_0} = l,$$

whence*

$$\overline{N}_0 = 0.5 + l + \sqrt{0.25 + l + 2(\overline{N}_b + \overline{N}_n)}. \qquad (10)$$

*As in the case of going from Eq. (7) to Eq. (8), the accuracy of Eq. (10) is increased by replacing 1 by 1 – 0.5.

It may readily be shown that the dependence $\overline{N}_0 = f(\overline{N}_b)$ cannot have the same form for different values of l even if the difference in l is partially compensated for by a difference in $\overline{N}_n$. Hence in principle it is possible to determine values of l and $\overline{N}_n$ for the system which will satisfy the conditions assumed above. These values may be determined from experimentally obtained characteristic curves of the form $c\overline{N}_0 = f(c\overline{N}_b)$, the scale of which, i.e., for which the coefficient of effective absorption, is unknown.

In conclusion it is necessary to make still another remark. In a number of works an approximate fluctuation criterion of the form of (3) is used for the threshold not only for a "simple" single-element receiver (for example, a photoelement), in which the signal or noise is registered simultaneously from the entire receiver, but also for complex multielement receivers. Such works are, for example, those of Rose[2] and Luisov,[3] which deal with the quantum theory of the discrimination properties of the eye and which are based on the ideas of Vavilov and Lebedev. The more accurate criterion (4) permitted us to explain in a previously published work[4] such rules of vision as the dependence of the threshold on the actual contrast and on the extent of the irradiating spot. The sensitivity threshold of multielement receivers has undoubtedly a fluctuating nature. Nevertheless, both the threshold criterion and the relationships obtained with its help must, strictly speaking, differ from those given above. The theory of the threshold of multielement receivers must be treated as a separate case.

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INTENSITY RATIO OF THE LUMINESCENCE BANDS OF ZnS:Mn AND ZnS:Ag:Mn PHOSPHORS AS A FUNCTION OF THE DENSITY OF CATHODOEXCITATION AND PHOTOEXCITATION

Yu. V. Voronov

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It is known[1-3] that the composition of the radiation of a phosphor with several activators varies with the density of excitation. Few papers,[4,5] however, have been devoted to a comparative study of this effect as between electron beam and light excitation. We have made such a comparison and have shown that certain peculiarities are observed under cathodoexcitation.

To perform the measurements, we used an arrangement which allowed us to use current densities from 10^{-9} up to 10^{-1} amp/cm² and accelerating voltages up to 35 kv. The luminescence spectra were measured photoelectrically. A PRK-4 lamp was used for photoexcitation, the excitation intensity being varied by means of wire mesh screens. The phosphors were baked for 30 min at 850°C. The manganese concentration C_{Mn} was 10^{-3}, 1.5×10^{-3}, 3×10^{-3} and 10^{-2} gm/gm; the flux was NaCl(2%) and the screen thickness ~4μ.

VARIATION OF THE LUMINESCENCE SPECTRA OF ZnS:Mn AND ZnS:Ag:Mn PHOSPHORS WITH THE DENSITY OF CATHODOEXCITATION

Figure 1 shows the luminescence spectra of the phosphors under cathodoexcitation. It can be seen that the blue band becomes weaker as the Mn concentration increases; a band appears with a maximum around 580-590 mμ. The position of the blue maxima in ZnS and ZnS:Ag phosphors does not vary with the introduction of Mn.

We obtained the luminescence spectra of ZnS:Mn (3×10^{-3} gm/gm) and ZnS:Ag (10^{-4}):Mn (1.5×10^{-3} gm/gm) phosphors as a function of current density at constant accelerating voltage. The curves in Fig. 2, a-d, represent the intensity in the maxima of the activator bands of ZnS:Ag:Mn phosphors as a function of current density. It is easily seen that the intensity of the blue band decreases gradually as C_{Mn} increases, while the luminescence of the Mn band increases. For a Mn concentration of 10^{-2} gm/gm, the blue band disappears almost completely. The saturation of the intensity of the manganese band with concentration is much less pronounced. A marked dependence of the luminescence color on current density is observed in a narrow range of activator concentrations (Fig. 2, c)(in the ZnS:Ag:Mn phosphor for a silver concentration around 10^{-4} gm/gm and 1.5×10^{-3} for manganese, in the ZnS:Mn phosphor for a Mn concentration of 3×10^{-3}). The luminescence of one of the bands predominates at other concentrations. Our data on activator interaction under cathodoexcitation agree qualitatively with those which Levshin[2,3] obtained in a study of photoexcited ZnS:Mn phosphors. Figure 3 shows the spectra of ZnS:Ag (10^{-4}):Mn phosphors for different Mn contents. Table 1 contains the data on the variation of the relative energy yield (B) of the luminescence of ZnS:Ag:Mn phosphors (B_0 is the sum of the bands, B_1 is the yellow band, and B_2 the blue band).

The relative energy yield was determined from the area of the luminescence spectra. The data show that

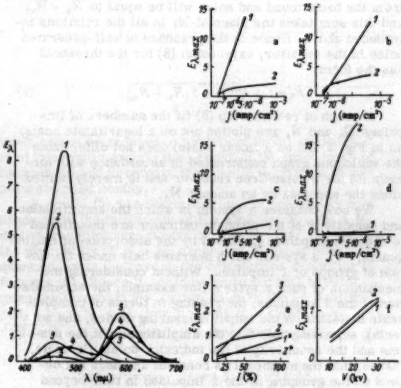

Fig. 1 Fig. 2

Fig. 1. Luminescence spectra of ZnS:Mn:Ag phosphors under cathodoexcitation (V = 15 kv, $j = 7 \times 10^{-7}$ amp/cm²). Curve 1—ZnS; curve 2—ZnS:Ag (10^{-4}); curve 3—ZnS:Ag (10^{-4}):Mn (1.5×10^{-3}); curve 4—ZnS:Mn (3×10^{-3}); curve 5—ZnS:Ag (10^{-4}):Mn (3×10^{-3}). The points on curve 4 were placed only to bring it out more.

Fig. 2. Curves giving the intensity of luminescence of ZnS:Mn:Ag phosphors at the maxima of the activator bands as a function of the following: current density (a-d), intensity of the exciting light (e), and accelerating voltage (f). Curve 1—luminescence of the blue band; curve 2—Mn luminescence. Figures a-d: V = 15 kv. Mn concentration (gm/gm): a—1×10^{-3}; b—1.5×10^{-3}; c—3×10^{-3}; d—1×10^{-2}. Figure e—wavelength of the exciting light (in mμ): curves 1,2—365; curves 1*,2*—313. Figure f—$j = 7 \times 10^{-7}$ amp/cm².

as the Mn concentration increases, the yield of the blue band decreases while that of the Mn band increases. The total luminescence yield of the ZnS:Ag:Mn phosphor decreases, goes through a minimum at a 1.5×10^{-3} gm/gm Mn, and then starts to increase. At a Mn concentration of 10^{-2} gm/gm, the phosphor luminescence becomes almost entirely due to manganese; its yield reaches a value characteristic of the ZnS:Ag (10^{-4} gm/gm) phosphor. An analogous behavior with regard to the energy yield is observed at other current densities as well.

Table 1

B	c_{M_n} (gm/gm)				
	0	$1 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
B_0	1055	483	360	415	1060
B_1	—	145	218	370	1035
B_2	1055	335	181	37	20

Figure 2, f shows the intensity of band luminescence at the maximum as a function of the accelerating voltage. An increase in the intensity of the activator band is observed for increasing voltage with almost no change in the ratio of the intensities of yellow and blue luminescence.

ESTABLISHMENT OF AN EMPIRICAL FORMULA TO REPRESENT THE RATIO OF THE INTENSITIES OF THE EMISSION BANDS OF ZnS:Ag:Mn AS A FUNCTION OF EXCITATION DENSITY

Luminescence spectra were taken of ZnS:Ag:Mn phosphors excited by 365 and 313 mμ light of different intensities. Figure 2, e shows the intensities of the blue and orange maxima as functions of the intensity of the exciting light. Comparing Figs. 2, b and 2, e we see that the activator bands show the same qualitative behavior under excitation by light and by an electron beam. Table 2 contains the values of the intensity ratio $K = E'_{\lambda_{max}}/E''_{\lambda_{max}}$ at the maxima of the yellow ($E'_{\lambda_{max}}$) and blue ($E''_{\lambda_{max}}$) activator bands as a function of the intensity of the exciting light.

Table 2 shows that the magnitude of the ratio K is independent of the wavelength of the exciting light. Table

Table 2

	$\lambda = 366$ (mμ)				$\lambda = 313$ (mμ)			
I (%) . .	12.5	25	50	100	12.5	25	50	100
K . . .	1.99	1.17	0.712	0.418	1.91	1.21	0.712	0.450
lg K . .	0.30	0.07	1.85	1.62	0.29	0.05	1.85	1.65

3 contains values of K and log K corresponding to cathodoexcitation (V = 15 kv) for different values of the current density j.

Table 3

j (amp/cm²)	$2.5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$9 \cdot 10^{-7}$	10^{-6}	$1.5 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$5 \cdot 10^{-6}$
K . . .	1.96	1.51	1.16	1.08	0.85	0.714	0.60	0.415
lg K . .	0.29	0.18	0.06	0.03	1.93	1.85	1.78	1.62

Figure 4 shows a log-log plot of K as a function of the exciting light (line 1) and of current density (line 2). Both cases satisfy the simple empirical relation

$$K = A \cdot I^{-\alpha},$$

where I stands for either the intensity of the exciting light or the current density and A and α are constants. For the given sample $\alpha_p = 0.72$ for photoexcitation and $\alpha = 0.54$ for cathodoexcitation. The data show that the straight lines log K = f(log I) corresponding to excitation by 366 and 312 mμ, respectively, do coincide. A comparison of the flux of the exciting light rays and of a Hefner candle has shown that the 366 mμ radiation was four times as intense as the 312 mμ radiation. By also taking into account the fact that the absorption coefficient of the phosphor is much higher at 312 mμ than at 265 mμ, we may assume that equal values of K at photoexcitation are obtained for approximately equal excitation states of the phosphor. It was of great interest to compare the excitation states of the phosphor characterized by equal values of the ratio K for different methods of excitation. Such a comparison has shown that the amount of energy entering the phosphor for cathodoexcitation was 30 times as large as for excitation by 312 mμ light, i.e., the same values of K were obtained for a much higher density of the absorbed energy. The slope of the curve log K = f(log j) for electron excitation also differs markedly from the slope for photoexcitation.

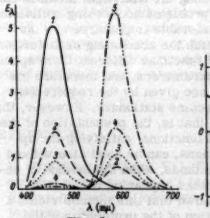

Fig. 3

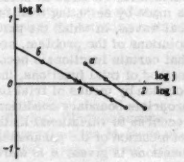

Fig. 4

Fig. 3. Luminescence spectra of ZnS:Ag (10^{-4}):Mn phosphors under cathodoexcitation (V = 15 kv, $j = 7 \times 10^{-7}$ amp/cm²). Mn concentration (in gm/gm): curve 1—0; curve 2—1×10^{-3}; curve 3—1.5×10^{-3}; curve 4—3×10^{-3}; curve 5—1×10^{-2}.

Fig. 4. Ratio of intensities of activator bands as a function of current density j and the exciting light intensity I. Curve a—excitation by 365 and 313 mμ radiation; curve b—excitation by an electron beam.

The observed difference in the interaction of the blue and orange bands for photoexcitation and cathodoexcitation constitutes a further specific distinction of phosphor luminescence under the action of cathode rays.

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THE THEORY AND CALCULATIONS OF COLLISIONS OF SLOW ELECTRONS WITH ATOMS

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In the quantum collision theory, when the method by Born based on the perturbation theory is no longer applicable, a correct accounting of distortions of the incident and scattered waves by the scattering system becomes very essential. Among the analytical methods for approximate solutions of problems concerning collisions of slow particles, of considerable importance are the variational methods in which the accounting of distortions is made by selecting trial functions different from spherical waves, in which the parameters, and therefore the solutions of the problem, are given by the requirement that certain functionals become stationary. However, the method of trial functions, that is, the presentation of the solution by means of trial functions, satisfying the appropriate boundary conditions, can be used also without recourse to variational methods, when the method of determination of the parameters appearing in the trial functions is given. It is shown that this method yields a sufficiently accurate solution of the problem, and the stability with respect to changes of the form of the trial functions is established. Calculation methods of this kind (for instance, the method by Galerkin and Krylov[1]) are widely used in many branches of mathematical physics, but have not been used yet in the quantum theory of collisions, although the number of methods for solution of problems concerning collisions of slow particles is very limited, and these methods are very cumbersome.

A very simple new method can be suggested for the solution of collision problems, which is based on utilization of trial functions. In this method, the parameters of the trial functions are determined without the condition of stationariness of the functionals which is characteristic of the variational methods, and without the orthogonality relations used in the methods by Galerkin and Krylov. We shall show some procedures for parameter determination in the trial functions by using this method. One of the procedures for the determination of the mentioned parameters is based on the consideration of the solution behavior for small r.

Let us consider first the problem of collisions of slow particles without taking exchange into account. In this case the trial function is substituted in the Schrödinger differential equation for the wave function of the scattered particle, and then it is developed in a power series in r. By equating to zero the coefficients of terms of equal powers of r, we obtain an infinite system of algebraic equations.

If the exact solution were included in the subset of the trial functions, the resulting infinite system of equations would be identically satisfied. However, in the actual calculations with n parametric trial functions, the Schrödinger equation is satisfied only for small r, and therefore in the infinite system only the first n equations are considered, and the latter are used for the determination of n parameters of the common functions.

In the problems concerning collision of particles with consideration of exchange, it is necessary to calculate first the wave function for small r by the method of Drukarev (M.D.),[2] which is relatively easy to do. The parameters contained in the trial function are determined then from the system of equations obtained by equating the coefficients of equal powers of r in the series development of the trial function, and of the M.D. function. By means of such an expansion method one can determine any number of parameters contained in the trial function.

Another method for the determination of parameters, which is not connected with series expansion in small r, can be illustrated by the simple example of elastic scattering. We introduce a regular one-parametric trial function

$$f_s(r) = u_l(r) + q_l B_l(r), \tag{1}$$

$$f_s(r) \underset{r\to\infty}{\sim} \frac{1}{k}\sin\left(kr - l\frac{\pi}{2}\right) + q_l e^{i\left(kr - l\frac{\pi}{2}\right)}, \tag{2}$$

where q_l is the amplitude to be determined, which is the only unknown parameter, $B_l(r)$ is the known function, and $u_l(r)$ is the plane wave.

On the other hand, the same amplitude satisfies the equation

$$q_l = -\int_0^\infty u_l(r)\, V(r)\, f_s(r)\, dr. \tag{3}$$

Substituting (1) and (3), and solving for q_l, we easily obtain the solution of the problem.

The conducted investigation has demonstrated that this solution is closely related to the solutions by variational methods based on the Hulthen functional, and relations were obtained connecting these solutions. Furthermore, the relation with the M.D. solution was clarified, and it was shown that a calculation method of this kind can be interpreted as a direct generalization of the quantum theory of transitions for the range for nonweak interactions by the method of trial functions. A generalization which considers exchange is trivial, and involves a simple substitution of (3) by an equation for q_l taking exchange into account.

Other methods for determination of the parameters of the trial functions can be obtained by substitution of the trial function not only in the integral equation for the scattering amplitude, but also in other relations connecting the wave function with the scattering field, for instance, in the virial expression.[3] In calculations with multiparametric trial functions one can use any combination of the above considered methods for the determination of the parameters of the trial functions.

With the suggested method calculations were made of the S-cross section of the elastic scattering of slow electrons by atoms of hydrogen, helium, and mercury without considering the exchange, S-, P-, D-, and F-scattering cross sections of slow electrons by atoms of calcium and mercury without consideration of exchange, as well as the excitation of the 2S level of the hydrogen atom by electron collision. Furthermore, the triplet scattering of neutrons by protons was calculated for a scalar exponential potential of interaction, with $k \to 0$. In all cases when it was possible, a comparison was made with more rigorous methods of calculation, and

with the experimental data, and a good accuracy of the method and a high stability of the solution with respect to changes of the form of the trial functions was proven.

In order to check further the accuracy of the method, calculations were made of the electron scattering in simple fields (of a rectangular potential well, and of an exponential field), for which a rigorous solution could be obtained analytically, and this solution was compared with the approximate solution. In addition, the convergence rate of successive iterations was investigated; also the accuracy of the wave functions, the stability of solutions with respect to the form of the trial functions, and so forth. Numerous calculations have shown that the suggested method yields a sufficiently good accuracy and stability of solution, being at the same time considerably simpler than the existing methods of calculation, that is, the variational methods[1] and M.D.[2]

For practical purposes it is of considerable interest to obtain simple analytical approximations for the effective cross sections, scattering amplitudes, etc. These quantities can also be obtained by means of the suggested method, if the trial functions are constructed not in the $\vec{r}$-space, but directly in the $\vec{k}$-space, that is, to make assumptions concerning the amplitude in question from general considerations as an explicit function of $\vec{k}$, with indefinite parameters. These parameters are determined from a system of equations which is obtained when the trial amplitude and the M.D. amplitude, first calculated for small values of $\vec{k}$, are developed in a power series in k, and the coefficients of equal k powers are equated.

Another convenient method for determining parameters of the trial amplitudes is based on certain restrictions which, as it was shown, are imposed by the unitariness of the scattering operator upon the coefficients of the power series of the scattering amplitude for small k. It can be shown (on the basis of the unitariness of the scattering amplitude) that the real and the imaginary parts of these coefficients are connected by a recurrent relation which is used for the determination of the parameters of the trial functions. Calculations of the elastic scattering of S-electrons by atoms of helium and mercury have confirmed the possibility of obtaining in this way simple analytical approximations for the effective cross sections.

It should be mentioned that the specificity of the method is not necessarily connected with the collision theory, and that it can be effectively used, for instance, for the solution of the quantum mechanical problems of a discrete spectrum. This statement was confirmed by direct calculations of wave functions and energy levels of hydrogen and helium atoms, of heliumlike ions and deuterium.

The sufficiently high accuracy of the suggested method, its simplicity, and the favorable experience of a similar approach in solving problems in other branches of mathematical physics, permit one to hope that the method will be a useful supplement to the existing methods of calculation.

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THE TRANSFER OF ELECTRONIC EXCITATION ENERGY WITH THE AID OF A VIRTUAL EXCITON MECHANISM

V. M. Agronovich

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In order to study the properties of polystyrene-base scintillators with luminescent impurity additives, it is essential to study the transfer mechanism of electronic excitation energy between impurity molecules. Under these conditions, in addition to the transfer mechanism involving direct interaction between impurity molecules (e.g., dipole-dipole interaction[1]), it is of definite interest to consider transfer processes based on a virtual exciton mechanism. Let us consider this problem in greater detail.

Let us assume that the molecules A and B are placed near the n-th and m-th segments of a long polymer chain. The complete Hamiltonian of the system is written in the form

$$H = H_0 + H_a + H_b + V_{ab} + \sum_n (V_{an} + V_{bn}), \qquad (1)$$

where the Hamiltonian of the polymer chain is

$$H_0 = \sum_{l=1}^{N} H_l + \sum_{k<l} V_{kl};$$

H_a and H_b are the Hamiltonians corresponding to the isolated molecules A and B; V_{an} and V_{bn} are the operators for the interaction between molecules A and B and the n-th segment of the polymer chain; V_{ab} is the interaction operator between molecules A and B.

Let us assume that the interaction between molecules A and B and the polymer does not lead to the appearance of new chemical bonds. Under these conditions the role of the interactions V_{ab}, V_{an}, and V_{bn} can be treated within the limits of perturbation theory.

The wave functions of the initial and final states of the system are determined as follows (we neglect the intermolecular exchange of electrons):

$$\left.\begin{aligned} \Psi_{\text{initial}} &= \varphi_a^* \varphi_b^0 \prod_n \varphi_n^0, \\ \Psi_{\text{final}} &= \varphi_a^0 \varphi_b^* \prod_n \varphi_n^0. \end{aligned}\right\} \qquad (2)$$

In this expression φ^0 and φ^* are the wave functions corresponding to the ground and excited states of the isolated molecules A and B or of one of the segments of the polymer. The probability of the transfer of electronic excitation energy from molecule A to molecule B by

direct interaction is determined by the following equation:

$$W_{ab} = \frac{2\pi}{\hbar}\left|\int \Psi^{*}_{\text{final}} V_{ab} \Psi_{\text{initial}} d\tau\right|^2 \rho(E_{\text{final}}) \equiv \frac{2\pi}{\hbar}|M_{ab}|^2 \rho(E_{\text{final}}), \quad (3)$$

where the functions Ψ_{final} and Ψ_{initial} correspond to one and the same energy, and $\rho(E_k)$ is the density of final states. On the other hand, the probability of transitions by means of intermediate states can be expressed in the following way:

$$W'_{ab} = \frac{2\pi}{\hbar}\left|\sum_{s} \frac{M_{Hs}M_{sb}}{E_{\text{initial}} - E_{\text{final}}}\right|^2 \rho(E_k). \quad (4)$$

For simplicity we shall only consider the interaction of molecules A and B with the nearest segments of the polymer chain. In addition, note that in the case under consideration it suffices to consider as intermediate states of the system those states in which molecules A and B are in the ground state and one of the excitons whose energy band is closest to the excitation energy of the molecules A and B is propagating along the chain.

The wave function of the exciton state of the polymer chain is written in the form:

$$\Psi_q \equiv \Psi_q = \frac{1}{\sqrt{N}} \sum_n e^{iqnd} \Phi_n, \quad \left(-\frac{\pi}{d} \leqslant q \leqslant \frac{\pi}{d}\right),$$

where

$$\Phi_n = \psi'_n \prod_{m \neq n} \psi^0_m.$$

The energies $E(q) = E'_0 + \varepsilon(q) = 2M \cos qd$ correspond to this state if one considers only interactions with nearest neighbors. Here,

$$M = \int \psi'^{0}_{n} \psi^{0}_{n+1} V_{n,n+1} \psi^{0}_{n} \psi'_{n+1} d\tau.$$

For the sake of simplicity, further calculations will be made using the effective mass approximation for the excitons. In this case, one assumes that

$$E(q) = E_0 + aq^2, \quad \frac{\pi^2}{d^2} = 4M.$$

Let us assume that the width of the exciton band is small in comparison to the energy difference $|E_H - E_0|$. In this case, after simple calculations we arrive at the expression

$$\left|\sum_{s} \frac{M_{Hs}M_{sb}}{E_H - E_s}\right| \simeq \frac{2|a||M_{aa}||M_{ab}|}{(E_H - E_0)^2 (n-m)^2 d^2}.$$

By comparing Eqs. (3) and (4), it follows that the ratio of probabilities is equal to

$$\frac{W'_{ab}}{W_{ab}} = \frac{4a^2 |M_{aa}|^2 |M_{ab}|^2}{|M_{ab}|^2 (E_H - E_0)^4 (n-m)^4 d^4}.$$

Let us assume that transitions from the excited state of the molecules A, B, and n to the ground state are allowed in the dipole approximation. In this case

$$|M_{ab}|^2 = \frac{|\overline{M}_{ab}|^2}{z^3 (n-m)^3},$$

where $|\overline{M}_{ab}|^2$ is the square of the modulus of the matrix element for a separation between molecules A and B equal to the constant of the polymer chain and $\varepsilon(\omega)$ is the dielectric constant of the medium. By assuming, for the sake of simplicity, that the moduli of the matrix elements M_{aa}, M_{ab}, and M_{nb} are approximately equal, we find that

$$\frac{W'_{ab}}{W_{ab}} = \frac{4a^2 (n-m)^2}{\pi^4} \left(\frac{|M_{aa}|}{E_H - E_0}\right)^2 \left(\frac{\pi z^2}{d^2 (E_H - E_0)}\right)^2.$$

The matrix elements $|M_{aa}| \approx 0.05$ ev/cm,[2] $\varepsilon \approx 3$, If one assumes a value of 0.5 ev for $|E_H - E_0|$, we conclude that $W'_{ab} > W_{ab}$ for $|n - m| > 40$. Thus, the energy transfer mechanism which we have been considering can become important in media of the plastic scintillator type at sufficiently low impurity concentrations. The role of this mechanism increases as the dielectric constant ε increases.

In conclusion, we note that the electronic excitation energy transfer mechanism described above turns out to be important in media in which an energy is transferred through triplet levels.[3] This is connected with the fact that in this case, the probability of a direct transfer W_{ab} decreases, roughly speaking, exponentially with distance (overlap integrals) while the probability of transfer by means of the virtual exciton mechanism, as before, remains proportional to $\sim 1/r^4$.

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HIGH-SENSITIVITY MODULATION PHOTOMETER

A. Yu. Borisov

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The present note describes a photometer in which a direct current flowing through a photomultiplier (PM) is changed, by means of a low-frequency voltage applied to one of the dynodes, into an alternating current of twice the applied frequency. This frequency doubling allows the signal to be filtered from stray induced currents.

As is well known, the sensitivity of presently used photometers in which the photomultiplier is not cooled is limited by the magnitude of the dark current. In good photomultipliers with cesium antimonide photocathodes the magnitude of the thermal dark current from the photocathode may be of the order of 10^{-15} amp or even smaller, which for a current multiplication factor of $M = 10^5$ leads to an anode current of magnitude $I_a = 10^{-10}$ amp. However, this is only one of the components of the dark current. (This question is considered in detail in reference 1.) Actually, since a potential difference $\approx 10^3$ volts is applied between the anode and the cathode of a photomultiplier, while the isolation resistance between them is (for tubes of the type FEU-19, FEU-22 and others) of the order of 10^{11} ohms, there is a leakage current flow $\approx 10^{-8}$ amp at the anode. If the output of the

circuit is fed to a dc amplifier (for example, an electrometer circuit), then the instability of this current will obviously determine the real sensitivity of the photometer.

The modulation photometer proposed below permits the elimination of the effect of leakage currents and permits an increase in the order of the sensitivity of the photometer for weak light inputs. The idea of the method is shown in the diagram given in Fig. 1. For a change in the potential of one of the intermediate dynodes ∂_n with

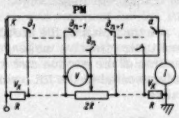

Fig. 1. Diagram showing the idea of the method.

respect to its neighbors (∂_{n-1} and ∂_{n+1}) the sensitivity of the photomultiplier changes (Fig. 2). This effect was used by the author and Tumerman for heterodyning the photomultiplier signal.[2]

The voltage on the sixth dynode of an FEU-17 was varied from zero to a value equal to twice the interstage value, with constant light input to the photocathode. During this process the amplification factor of the photomultiplier varied approximately symmetrically with respect to the value corresponding to the normal interstage voltage, for which the photomultiplier has maximum amplification factor. Thus, if in addition to the constant interstage voltage, a low-frequency alternating voltage is also applied to the dynode, then, as a result of the symmetry of the curve, the photomultiplier current will be modulated with twice the applied frequency. The phenomenon of frequency doubling has a decisive significance, since there is a stray capacitance of the order of a picofarad between the dynode and the anode. The modulating voltage can reach the output of the photomultiplier through this stray capacitance and give a parasitic signal exceeding the measured signal by several orders of magnitude.

Following this frequency doubling, the signal at the output of the photomultiplier is amplified by means of a tuned amplifier which filters out the "induced" current from the signal, the frequency of which has been doubled. It is evident that the stray currents through the body of the tube will not be modulated and hence will not pass through the amplifier. The sensitivity of such a circuit is limited only by the shot effect and may be made very high. Moreover, the transformation of the signal into an alternating current allows the application of a lock-in detector as the output indicator. Application of such a detector still further increases the sensitivity of the system.

A block diagram of the apparatus is shown in Fig. 3. The second harmonic of the generator frequency must be effectively suppressed (for example, by use of a push-pull output), since it would reach the anode of the photomultiplier through the stray capacitance and would give a spurious signal coinciding in frequency with the useful signal. The modulation frequency selected is not higher than some few tens of cycles per second, in order to insure that the amount of second harmonic induced at the anode of the photomultiplier will be negligibly small.

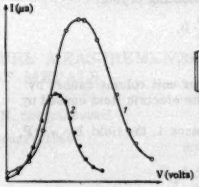

Fig. 2

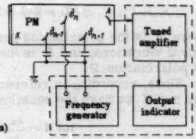

Fig. 3

Fig. 2. Dependence of the sensitivity of the photomultiplier on the magnitude of the voltage applied to one of the interstage dynodes.

Fig. 3. Block diagram of the photometer.

The sensitivity of the apparatus is approximately an order of magnitude higher than the sensitivity of photometers using dc amplifiers and can detect as few as 50 photoelectrons per second from the photocathode of the photomultiplier.

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ON THE SPIN LATTICE RELAXATION OF EXCITONS IN AN IONIC CRYSTAL

V. N. Paranichev

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As a result of the interaction between the exciton spin and optical lattice vibrations, transitions with the emission or absorption of a phonon can occur between a state of a given multiplicity and a state with another multiplicity. In this paper, the lifetime of an exciton with respect to a transition of this type is calculated. For this purpose we start from Maxwell's equations for the magnetic field in a nonconducting crystal

$$\text{rot } \mathbf{H} = \frac{1}{c}\dot{\mathbf{D}},$$

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P},$$

where $\mathbf{P}$ is the polarization per unit volume caused by optical vibrations, and $\mathbf{E}$ is the electric field caused by the polarization $\mathbf{P}$.

Since, according to reference 1, the field $\mathbf{E} = -4\pi\mathbf{P}$, then for $\mathbf{H}$ we have the equation

$$\text{rot } \mathbf{H} = \frac{4\pi}{c}\dot{\mathbf{P}}_{\perp},$$

where $\mathbf{P}_{\parallel}$ and $\mathbf{P}_{\perp}$ are the longitudinal and transverse components of the polarization. The expression for the total polarization $\mathbf{P}$, taken from reference 2, is

$$\mathbf{P}(r) = \frac{Ze}{\sqrt{M}\,2a^3\sqrt{N}} \sum \mathbf{e}_j \left(a_{qj} e^{iqr} + a^{*}_{qj} e^{-iqr}\right).$$

Here Ze is the ionic charge, $M = (M_+M_-)/(M_+ + M_-)$ is the reduced mass (M_+ and M_- are the masses of the positive and negative ions respectively); N is the number of elemental cells in the crystal; $2a^3$ is the volume of an elemental cell; q is the wave vector, and $\mathbf{e}_j$ is the polarization vector of the vibrations.

The index j for $j = 1,2$ denotes the two transverse branches, whereas $j = 3$ refers to the longitudinal branch. The amplitude operators a_{qj} and a^{*}_{qj} satisfy the relation

$$\left[a_{qj} a^{*}_{q'j'}\right] = \frac{\hbar}{2\omega}\,\delta_{qq'}\delta_{jj'}.$$

In what follows, we shall use, in place of e_{qj}, the dimensionless amplitude

$$a_{qj} = \sqrt{\frac{2\omega}{\hbar}}\, a_{qj},$$

where ω is the limiting value of frequency in the longitudinal branch. The limiting frequencies in the transverse vibration branches are assumed to be equal to ω. Since the goal of this calculation is the evaluation of the order of magnitude of the transition probabilities, such an assumption is permissible. The expression for the operator derivative with respect to time on the transverse part of the polarization is obtained by multiplying $\mathbf{P}_{\perp}$ by $i\omega$.

If we solve the equation for the magnetic field in the same way as in reference 3, we obtain

$$\mathbf{H} = \frac{4\pi}{c}\,\frac{Ze}{\sqrt{M}\,2a^3\sqrt{N}}\sqrt{\frac{\hbar\omega}{2}} \sum_{q,\,j=1,2} \frac{\mathbf{e}'_j}{q}\left(a_{qj} e^{iqr} + a^{*}_{qj} e^{-iqr}\right),$$

where $\mathbf{e}'_1 = \mathbf{e}_2$ and $\mathbf{e}'_2 = -\mathbf{e}_1$ (to the accuracy of an unimportant phase factor). We take the following expression as the perturbation

$$\mathcal{H}' = \frac{e\hbar}{\mu_1 c}\,\hat{\mathbf{S}}_1\mathbf{H} - \frac{e\hbar}{\mu_2 c}\,\hat{\mathbf{S}}_2\mathbf{H},$$

where $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ are the spins of the electron and hole and μ_1 and μ_2 are their effective masses.

The wave function of the exciton and the lattice vibrations can be represented in the following form in the zeroth approximation.

$$\Psi = \frac{e^{i\mathbf{K}\mathbf{R}}}{\sqrt{V}}\,\varphi^{(S)}_{nl}(r)\,\chi_s \prod_{q,j} \Psi^{n^0_{qj}}_{q,j},$$

where $\mathbf{K}$ is the wave vector of the exciton as a whole; $\mathbf{R}$ is the coordinate of the center of gravity; $\mathbf{r}$ is the relative motion coordinate; V is the volume of the crystal; n^0_{qj} is the occupation number of the lattice oscillators, χ_s is the spin function of the electron and hole; $\varphi^{(S)}_{nl}(\mathbf{r})$ is the wave function of internal motion in the exciton, and nl is the quantum number. According to the data in references 4 and 5, Ψ depends on the total spin of the exciton which is indicated by the index S.

The transition probability calculated from perturbation theory is

$$W = \frac{2\pi}{\hbar}\,|\mathcal{H}'|^2\,\rho_E,$$

where the density of states is

$$\rho_E = \frac{VM_1K'd\Omega}{8\pi^3\hbar^2},$$

where $M_1 = \mu_1 + \mu_2$; $\mathbf{K}'$ is the exciton wave vector after a collision with a phonon, and $d\Omega$ is the solid angle in which $\mathbf{K}'$ is located (the z axis is directed along $\mathbf{K}$, the wave vector of the exciton before collision with the phonon). For an exciton, which is found in the singlet state with internal motion quantum numbers nl and with the translational motion vector $\mathbf{K} = 0$, the probability (per sec) of a transition to the triplet state with the same quantum numbers nl (i.e., for the transition from a para-exciton to an ortho-exciton), and with the emission of a transverse optical phonon of wave vector q, is given by the expression

$$W = \frac{2\pi}{\hbar}\,B\,\frac{1}{q}\sum_{l_1}(-1)^{l_1} R^2_{nl_1} C^2_{l_1 nl},$$

where

$$B = \frac{4}{3}\,\frac{\pi^2 e^4 \hbar\omega M_1}{\mu_1^2 c^4 M 2a^3}\left(n^{*}_{qs} + 1\right).$$

The quantities R and C are determined by the expressions

$$R_{nl_1} = 4\pi \int j_{l_1}\left(\frac{\mu_2}{M_1}\,qr\right) R^S_{nl} R^1_{nl}\, r^2 dq,$$

$$C_{l_1 nl} = \int |Y_{lm}(\theta,\varphi)|^2\, Y_{l_1 0}(\theta,\varphi)\cdot \sin\theta d\theta d\varphi,$$

where j_{l_1} is the spherical Bessel function, and R^S_{nl} and R^1_{nl} are the radial parts of the internal motion wave function corresponding to the triplet and singlet states.

The wave vector q is determined by the conditions

$$E^1_{nl} - E^3_{nl} = \hbar\omega + \frac{\hbar^2 q^2}{2M_0}.$$

In the calculation of the transition probability nl → nl the summation index l_1 runs over all even numbers from 0 to 2l. For example, for the transition np → np, $l_1 = 0,2$; for the transition nd → nd, $l_1 = 0, 2, 4$, etc.[6] As is evident from the results of the calculation, the probability of transition with phonon emission becomes greater as the difference between corresponding para- and ortho- levels approaches the magnitude of the phonon energy. A value of 10^{-5} to 10^{-6} sec was obtained for the lifetime of an exciton with respect to flipping of the spin with simultaneous phonon emission. This is far greater than the lifetime with respect to fluorescence. In the event, however, that the exciton lifetime with respect to annihilation increases for any reason whatever, the mechanism described above can become effective.

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A METHOD FOR MAKING LOW-TEMPERATURE MEASUREMENTS OF THE OPTICAL CONSTANTS OF METALS

V. G. Padalka and I. N. Shklyarevskii

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Low-temperature measurement of the optical constants of metals in the infrared region of the spectrum is of obvious importance. Such measurements are quite simple in the case of metals having low conductivity.[1] Low-temperature measurements of the optical constants of metals having high conductivity have lagged, however, because of experimental difficulties. The optical constants of such metals can be reliably measured (especially at low temperatures) by using polarization methods in which light is repeatedly reflected from identical samples.[2-7] The special features of these methods must be considered in the design of the cryostat. Following is a description of a cryostat which is suitable for use with the methods of low-temperature measurement given in references 2 to 6.

The cryostat shown in Fig. 1 is housed in a copper cylinder (1) of 17 cm inside diameter, closed at the ends with vacuum sealed plates. Copper sylphons (2), soldered to the end plates, permit the test samples to be positioned within the evacuated region. The test samples (3) and (4) (in the form of films or solid layers of metal deposited on glass plates), 15 × 3 and 11 × 3 cm in size, are firmly attached with fasteners to the flat surfaces of the thin-walled copper reservoirs (5), which are cooled internally with liquid nitrogen. The coolant is supplied to the reservoirs through nickel-silver tubes (6). Three adjustment screws (7), the ends of which butt against the cryostat housing, are provided for orienting sample (4) parallel to sample (3). Sample (3) is moved laterally by turning nut (8). The flange of cylinder (9) is pressed into a groove in nut (8). The nickel-silver tube coming from the reservoir to which sample (3) is attached is soldered to this flange. The accuracy of axial motion of cylinder (9) is assured because the inside surface of cylinder (10) is lapped to fit the outside surface of cylinder (9). A key, which fits into the groove of cylinder (10), keeps the cylinder (9) from turning.

Light, after passing through the polarizer, enters the cryostat through window (11), undergoes multiple reflection between samples (3) and (4), and exits from the cryostat through window (12). Windows (11) and (12) are plane-parallel plates of sylvite (KCl) or rock salt. They are mounted on the cryostat with vacuum seals. Since

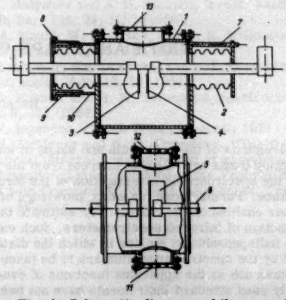

Fig 1. Schematic diagram of the cryostat.

the angle of incidence of the light falling on the windows is close to normal (less than 25°), the windows contribute little to the polarization of the light. The design of the cryostat and the dimensions of the windows (6 cm diam) make it possible to achieve any angle of incidence greater than 65°. The path of the light during adjustment of the samples can be observed in visible light through window (13).

The cryostat is first evacuated by a fore-vacuum pump; further evacuation is accomplished by sealing a carbon absorber to the body of the cryostat. This makes it possible to maintain a high vacuum in the cryostat (of the order of 5×10^{-6} mm Hg) for 10 to 12 hr while the latter is disconnected from the external vacuum system. The vacuum is controlled by means of a manometer connected to the cryostat. The surface temperature of samples is measured with a thermocouple.

The cryostat is mounted on a goniometer platform, which is equipped with a special carriage and three leveling screws. During adjustment of the equipment these screws are used to assure vertical positioning of the samples. The carriage permits axial movement of

the entire cryostat. A photograph of the setup is shown in Fig. 2.

Fig. 2. External view of the equipment. 1—body of cryostat; 2—carbon absorber; 3—manometric tube; 4—cup leading to German silver tube for adding liquid N_2; 5—carriage of cryostat; 6—adjusting screws; 7—analyzer (selenium pile); 8—bolometer.

With the cryostat described above, it is possible to make measurements using the methods given in references 8 and 9 if the larger sample is positioned over the center of the goniometer platform and the smaller sample is displaced to one side.

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WIDTH AND SHAPE OF INFRARED ABSORPTION BANDS

G. G. Petrash

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Measurements of the real width and shape of infrared absorption bands are of great interest from the point of view of the spectroscopic investigation of the structure of a substance. Furthermore, an exact knowledge of the band contour enables one to calculate or estimate the apparatus function of infrared spectrometers. Such estimates are indispensable in studies in which the distortions introduced by the spectral apparatus are to be taken into account, inasmuch as the apparatus functions of even the most widely used standard instruments have not been measured up to now.

Regrettably, very few measurements of the real width and shape of infrared bands have been carried out up to the present time. Accordingly, we have undertaken such measurements with the help of an apparatus of high resolving power. For the measurements we chose readily available substances which possess, as far as possible, narrow single absorption bands of a more or less simple shape. The preliminary selection of bands was carried out with the help of an AIKS-F4 apparatus.[1] All the bands investigated by us lie in the spectral region where an NaCl prism may be employed.

The final measurements were carried out on the double-beam grating spectrometer described earlier.[2] An echelette with 50 lines/mm was used in the first order. The spectrometer was calibrated by means of the NH_3 spectrum.[3-4] The apparatus made it possible to work with slits of $S \approx 0.4$-0.7 cm^{-1} at moderate scanning speed, which guaranteed that all the bands studied were recorded practically without systematic distortions. Constant-thickness cells of NaCl were used, their thickness being measured by interference in the empty cell. Most of the measurements were made without compensation for absorption by the cell. In addition, special measurements were carried out with two cells of different thickness in the different light beams (i.e., with compensation for absorption by the cell and reflection from its surface) in order to clarify the nature of the background absorption.* These measurements showed that the observed continuous background absorption is connected to a significant degree with the investigated substance itself. Accordingly, in working out the spectra the value of the absorption in the band was reckoned from the level of the background absorption, drawn in such a way as to be tangent to the "tails" of the band under study. The bands were recorded over an interval which exceeded the band width by a factor of 8-10. The substances investigated were first subjected to purification with the help of the methods usually used in molecular spectroscopy. In particular, special measures were taken for the purification and drying of pyridine. The precision of the measurements of the band width amounted to approximately 5%.

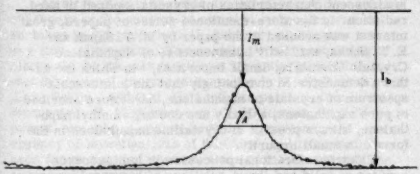
*V. Ya. Balakhanov took part in these measurements.

Substance	$\tilde{\nu}$ (cm^{-1})	λ (μ)	d (μ)	A_m (% above background)	a_m	γ_A (cm^{-1})	γ_D (cm^{-1})	Shape	2Q according to ref. 5
Naphthalene (solid)	1008	9.91	21.5	76	1.43	2.3	1.6	Sidebands Weak	1.8
Pyridine	1030.7	9.702	18	86	1.93	6.8	4.6	Sidebands Dispersion	
Pyridine	1147.4	8.715	18	54	0.76	8.4	6.9	Sideband	
Pyridine	1217.8	8.213	18	53	0.75	8.8	7.1		
Cyclohexane	903	11.08	40	74	1.36	8.2	4.5	Dispersion Sideband	5.0
Benzene	1038.8	9.845	10	68	1.13	12.5	8.9		
Acetonitrile	918	10.90	20	81	0.95	9.0	7.9	Asymmetry	

In the Table are given the following characteristics of the bands investigated: (1) the absorption $A_m = (I_b - I_m)/I_b$ and the optical density $D_m = \ln(I_b/I_m)$ at the band maximum, reckoned from the background line; (2) the width at the half-height of absorption γ_A and the width at the half-height of optical density γ_D; (3) the wavelength λ and the frequency ν of the band maximum; (4) the cell thickness d.

The last column of the Table gives, for comparison, the values of γ_D obtained for two bands in reference 5.

The experimental results show that, of the seven chosen bands, only two possess a simple shape very close to the dispersion shape with respect to both optical density and absorption at the d values which we used. These are the cyclohexane band $\nu = 903$ cm^{-1} and the pyridine band $\nu = 1147$ cm^{-1} (the Figure shows how well the circles which describe the dispersion contour coincide with the actual contour of the 1147 cm^{-1} pyridine absorption band).



Spectrogram of the pyridine absorption band $\nu = 1147$ cm^{-1}. Values of the dispersion function which approximates the band contour are marked by circles.

The remaining bands are also characterized by a slow falling-off of the intensity at the edges (similar to the wings of a dispersion band), but they possess, in addition, a marked asymmetry, or else they have weak side maxima, so that their shape cannot be described by a simple analytic function.

Of the bands considered, the two which have a dispersion contour may be conveniently used for the calculation of the apparatus function, since there are detailed tables comprising the dispersion function along with many others.[6,7] The remaining bands may be used for rougher estimates of the apparatus function. In addition to the measurements of the spectra of pure substances, a solution of pyridine in CCl_4 was also studied. The measurements showed that the width and intensity of the bands depend substantially on the concentration of the solution. The results of these measurements will be discussed in another place. Here we note only that, before this solution is used as a standard, more careful measurements of the band width as a function of concentration must be carried out. These questions will be the subject of further investigations.

The author expresses his appreciation to P. A. Bazhulin, and also to V. I. Malyshev and S. G. Rautian, for very valuable discussions of this work.

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CHRONICLE

THE EIGHTH CONFERENCE ON LUMINESCENCE

(Molecular Luminescence and Luminescence Analysis)

The Eighth Conference on Luminescence, convened by the Science Council on Luminescence of the Belorussian SSR Academy of Sciences and by the Physics Institute of the USSR Academy of Sciences, was held on October 19 through 24, 1959 in Minsk. The proceedings of the conference were handled in two sections: (1) Molecular Luminescence, and (2) Luminescence Analysis. About one hundred twenty papers were delivered at the conference, the majority in the first section. An outstanding feature of the conference was that a considerable portion of the papers presented was devoted to general problems: transformation of electron-excitation energy inside the molecules, properties of different types of secondary glow, processes of intra- and intermolecular exchange and of the transfer of electronic and vibrational energies, the effect of intermolecular interactions of different types on the spectral properties of molecules, and the problem of the connection between electronic and vibrational motion.

The first paper, by V. L. Ermolaev and A. N. Terenin, was devoted to the problem of intermolecular energy transfer in the triplet levels of complex molecules. The paper demonstrated the fruitfulness of extending the concepts of resonant energy transfer between molecules to intramolecular processes. In the paper by V. L. Ermolaev, I. P. Kotlyar, and K. K. Svitashev, entitled "Probability of Internal Conversion from the Fluorescent to the Phosphorescent Level in Naphthalene Derivatives" it was shown that introduction of naphthalene derivatives of atoms of heavy halogens into the molecule leads to a sharp increase in the probability of internal conversion from the singlet to the triplet level. Analogous results for phthalimide derivatives were obtained by V. A. Borgman, I. A. Zhmyreva, V. V. Zelinskii, and V. P. Kolobkov.

A paper by S. O. Mirumyants and B. S. Neporent presented new data on the conversion of vibrational energy of excited complex molecules upon their collision with molecules of different extraneous gases. It was shown

that the amount of energy transferred is determined by the Van-der-Waals interaction constants. The results of the investigation of intermolecular interactions of complex organic molecules in the gaseous phase, by using a method based on the influence of light gases on the intensity of electron absorption, were reported in a paper by V. P. Klochkov. Related to these papers are also those by N. A. Borisevich and V. V. Gruzinskii, entitled "Electron Spectra of Vapors and Solutions of Antraquinones," and by N. A. Borisevich and V. A. Tolkachev, entitled "Temperature Dependence of the Fluorescence Yields of Vapors of Complex Molecules."

A series of papers by B. Ya. Sveshnikov, P. I. Kudryashov, V. I. Shirokov, and L. A. Limareva was devoted to the problem of migration of energy, concentration depolarization of fluorescence, and fluorescence of solutions of organic compounds, as well as sensitized fluorescence in solutions. A lively discussion was caused by the interesting known experimental fact, which contradicts the general concepts, that the degrees of depolarization of fluorescence and of delayed fluorescence are the same. Dealing with the same topic was the theoretical paper by Yu. A. Kurskii and A. S. Selivanenko, entitled "On the General Theory of Extinction of Luminescence of Solution by Impurities," in which an attempt was made to take diffusion in migration extinction into account in general form, and also the paper by V. L. Levshin, E. G. Baranova, and L. V. Krotova, entitled "Transfer of Excitation Energy to Associates in Luminescent Solutions of Dyes and the Character of the Binding Forces of the Associates," as well as that of L. V. Levshin and V. A. Bocharova, entitled "Investigation of the Concentration Effects in Solutions of Certain Organic Compounds."

Considerable interest was aroused by the paper by A. N. Terenin and A. V. Shabel', entitled "Detection of Phototransfer of a Proton through the Luminescence Spectra." It was shown in the paper that the change in the fluorescence color produced by irradiating 9-(oxyphenyl) acridine in vacuum is a result of phototransfer of a proton. Starting with this premise, it is suggested that, in a compact layer, the 9-(oxyphenyl) acridine is in the oxo- and not in the oxy-form, as in the case of solutions.

The investigation of polarization properties of the luminescence of complex molecules in liquid and solid solutions was the topic of two papers by G. P. Gurinovich, A. M. Sarzhevskii, and A. N. Sevchenko.

Particular interest was aroused by a paper by E. V. Shpol'skii and L. A. Klimova, entitled "New Data on Spectra of Automatic Hydrocarbons at 20°C," devoted to further investigations of the phenomenon, discovered by the authors several years ago. In this phenomenon the electron spectra of the solutions of several automatic compounds in normal hydrocarbons, comprising under normal conditions an aggregate of broadbands with an unresolved fine structure, turn practically into line spectra in frozen-in solid solutions at the boiling temperature of liquid nitrogen or helium. The authors interpret the results obtained and show that this phenomenon can be used successfully as a method of investigating the vibrational structure of the electronic spectra of complex automatic compounds.

The use of the foregoing phenomenon for the investigation of the luminescence spectra of halide-derivatives of antraquinone and of thioindigo and its derivatives was the topic of papers by D. N. Shigorin, N. A. Shcheglov, and N. S. Dokunikhin and by R. N. Nurmukhamedov, D. N. Shigorin, and N. S. Dokunikhin. Other papers on this topic were by T. N. Bolotnikova, "Spectra of Certain Automatic Aldehydes and Ketones at Low Temperatures," A. Ya. Khesina, "Spectroscopy of Certain Derivatives of Pyrene in Frozen Solutions," and by S. G. Bogomolov, F. D. Pemova, and L. I. Kolosova "The Last Lines of the Spectrum of 3, 4-benzpyrene, Dissolved in Normal Hydrocarbons at Different Temperatures."

One plenary session and one of the sessions of the section on Molecular Luminescence were devoted in their entirety to research on luminescence and other characteristics of molecular crystals and solid solutions (A. N. Faindysh, M. T. Shpak, and E. F. Sheka; V. I. Gribkov and N. D. Zhevandrov; V. M. Agranovich and Yu. V. Konobeev; V. L. Broude and V. S. Medvedev; Ya. Ya. Kirs and A. I. Laisaar; M. I. Belyi and B. F. Rud'ko), and also certain problems of the theory of excitons and molecular crystals (V. M. Agranovich). In addition, a group of papers (Z. A. Chizhkova, I. M. Rozman, Yu. V. Naboikin, V. K. Dobrokhotova, and V. V. Uglanova; Sh. D. Khanmagametova, N. D. Zhevandrov, and V. I. Gribkov) was devoted to the investigation of scintillation properties of certain organic substances and different luminescent characteristics of crystals exposed to hard radiation. In the afore-mentioned series of papers, great interest was aroused in the paper by M. T. Shpak and E. F. Sheka, entitled "Luminescence of Naphthalene Crystals Containing Small Impurities," in which the authors demonstrated convincingly that the luminescent spectrum of crystals of naphthalene, heretofore ascribed to pure naphthalene, actually are due to β-methyl naphthalene, always present in crystalline naphthalene in the form of a small impurity.

Electron-vibrational processes in luminescence centers of solid and liquid solutions of mercurylike ions were considered in a paper by Ch. B. Lushchik, N. E. Lushchik, G. G. Liid'ya, and K. K. Shvarts.

Several papers were devoted to the question of the effect of the solvent on absorption and fluorescence spectra of organic compounds. The paper by A. S. Cherkasov cited new experimental data on the effect of a large group of solvents and of the temperature on the fluorescence spectra of acetylanthracenes. In a paper entitled "Dielectric Effects and Properties of Electron Spectra of Polyatomic Organic Molecules in Solutions," N. G. Bakhshiev showed that the results of the experiments are in satisfactory quantitative agreement with the deductions of the theory, relating the position of the spectra with the macroscopic characteristics of the solvent. Considerable experimental material regarding the positions of the fluorescence spectra of several aromatic compounds in a large number of solvents was given in the paper by I. A. Shmyreva, V. V. Zelinskii, V. P. Kolobkov, A. A. Kochemirovskii, and I. I. Reznikova. The foregoing papers raised a lively discussion concerning the problem of the nature of intermolecular forces causing the spectra to shift upon going from vapor to solution.

Included in the same group were papers by L. G. Pikulik and A. N. Sevchenko, entitled "Temperature Dependence of the Quantum Yield of Fluorescence of Certain Phthalimides in Various Solvents," by L. G. Pikulik and M. A. Solomakho, entitled "Effect of the Temperature on Electronic Spectra of Complex Molecules in Solutions," and also the paper by G. M. Kislyak, on "The Phosphorescence of Certain Solvents." The first of these papers reported the interesting experimental fact that in many solvents the quantum yield of glow increases with increasing temperature.

The theoretical papers delivered at the conference can be arbitrarily divided into two groups. The first includes papers by B. I. Stepanov and his co-workers, devoted to a study of different types of secondary glow and to a comparison of the classical and quantum-mechanical methods of analysis of the interaction of light with matter, and also the calculation of the contours of

the bands of complex molecules. The experimental physicists expressed great interest in the paper delivered by B. I. Stepanov, which convincingly demonstrated that neglect of the secondary light absorption and emission processes may lead to significant errors in the interpretation of the experimental data, particularly in the investigation of the duration of glow, the laws of damping of luminescence, etc. The second group of papers includes those devoted to the connection between the electronic and vibrational motion in molecules. M. A. Elyashevich in a paper entitled "Interaction between the Electronic and Vibrational Motions in Complex Molecules" showed that, starting with the most general considerations, one can subdivide in each system the electronic and vibrational motions, inasmuch as the kinetic energy of vibration of the nuclei comprises a small addition to the total energy of the entire system as a whole, and, consequently, the adiabatic approximation can be used in a theoretical analysis of this question.

An attempt at presenting a general quantum-mechanical theory of the spectra of complex molecules was undertaken in the paper by S. I. Kubarev, which gave rise to a lively discussion. The question of the probability of electron-vibrational transitions for a single oscillator was the topic of an interesting paper by K. K. Rebane, A. A. Rentel', and O. I. Sil'd. Those participating in the discussion—V. M. Agranovich, K. K. Rebane, B. S. Neporent, and others—pointed out the importance and urgency of investigations of this kind, and indicated the need for comparing the deductions of the theory with the experimental results.

The verification of the validity of a universal relation between the absorption and luminescence spectra, using a group of organic compounds as an example, was the topic of many papers. Particular interest attached to the paper by M. A. Alentsev, in which it was shown on the basis of careful measurement that, in the case of erythrosine solutions, this relation is satisfactorily fulfilled over a wide spectral region.

Several papers were devoted to the investigation of uranyl compounds.

Many authors considered the problem of spectroscopic investigations of the hydrogen bond (papers by D. S. Shigorin and his co-workers, and also by Yu. V. Naboikin, V. A. Zadorozhnyi, and L. A. Ogurtsova).

The effect of concentration of hydrogen ions on the fluorescence of the derivatives of naphthalene was considered in a paper by L. D. Derkacheva.

Several papers were devoted to processes of deactivation of excited states of complex organic molecules (E. A. Bozhevol'nov and V. V. Zelinskii and co-workers). Included in the same group were the papers by T. M. Vember and A. S. Cherkasov, on "The Effect of Extinction Fluorescence on Quantum Yields of Photochemical Conversions of Several Derivatives of Anthracene," and by V. S. Adamov and L. T. Kantradzhyan, "The Kinetics of the Monomolecular Glow Process."

In a paper by E. V. Anufrieva and A. D. Zaitseva, interesting data were reported on the changes in the phosphorescent properties of several polymers during their vitrification.

The last plenary session was devoted to the problem of a complete spectroscopic investigation of chlorophyll. Papers were delivered at this session by T. N. Godnev, R. V. Efremova, N. P. Ivanov, and L. A. Kravtsov, who reported on methods of investigating chlorophyll production, on optical properties of chlorophyll and pheophytin at low temperatures, on the quantum yield of chlorophyll in different solvents, and on the aggregation of molecules of chlorophyll and chlorophyllide. Considerable interest was attracted to the paper of A. A. Krasnovskii and S. S. Litvin, entitled "Investigation of the Luminescence of Leaves and of Model Systems."

The papers read at the four sessions of the second section were devoted to a wide circle of problems connected with the application of methods of luminescent analysis in a great variety of fields of science and engineering. These included the following problems: qualitative and quantitative determination of the contents of certain elements and organic compounds in mixtures of various composition, the development of new methods and the use of modern apparatus for analytical purposes, the use of luminescent analysis in biology and medicine and also in engineering and agriculture. As in the preceding conference, a large proportion of the papers delivered in the second section was devoted to the utilization of luminescent methods in biology and medicine (microscopy of biological objects and live organisms, diagnosis of various diseases in animals and humans, production of various medications, etc.). The transactions of the second section of the conference will be published separately by the Belorussian SSR Academy of Sciences.

As a whole, the Eighth Conference on Luminescence was held on a high scientific-theoretical level and demonstrated the successful and rapid development of the principal trends in this scientific field in our country. Characteristic of the Eighth Conference also was the high percentage of experimental and theoretical works performed by young scientists, who actively participated in the discussions on fundamental problems in luminescence. One must point out, however, one serious shortcoming—that, as noted particularly at one of the plenary sessions, not enough research is being performed as yet on spectroscopic and luminescent properties of molecules in the gaseous phase. Such work is being done at present only in two places—Leningrad (B. S. Neoporent) and Minsk (N. A. Borisevich).

In conclusion, mention should be made of the thorough preparation for the running of the conference, in the organization of which a large role was played by the staff of the Belorussian SSR Academy of Sciences and of the Belorussian State University.

N. G. Bakhshiev and S. O. Mirumyants

THE THIRD URALS SYMPOSIUM ON SPECTROSCOPY

In January 1960, the Third Urals Conference on Spectroscopy was held in Sverdlovsk. It was attended by more than 250 representatives of the higher institutions of learning, research organizations, and industrial laboratories in the Urals, and also by representatives from Moscow, Leningrad, Siberia, Kazakhstan, and the Ukraine. One of the features of the conference, absent in the preceding ones, was that in addition to a section on atomic spectroscopy, a section was also devoted to molecular spectroscopy. Eighty five papers were read dealing with atomic spectroscopy, while twenty five were delivered on molecular spectroscopy.

Some of the communications on atomic spectroscopy were devoted to processes occurring in arc discharges. Yu. A. Sherstkov considered in his paper the dependence of the total intensity of spectral lines on the concentration of the elements in a dc arc. I. G. Preobrazhenskii developed a new version of the use of reabsorption for the measurement of absolute concentrations of atoms in a plasma. A communication by N. S. Sventitskii was devoted to the role of electrode polarity in spectral analysis.

Processes that determine the character of the flow of material from the sample electrode into the radiating discharge cloud occupied a permanent place in the work of the conference. In a paper by A. B. Shaevich, devoted to a study of the connection between the physical-chemical state of an element in a metallic alloy and the intensity of its emission lines, it was deduced that under conditions when the temporal processes on the electrodes (such as sparking, diffusion, etc.) are excluded, the factor deciding the character of flow is the binding energy of the particles in the crystal lattice. Considerable interest was aroused by communications from M. N. Shtutman and his co-workers on peculiarities of the entry of the electrode material into the discharge when operating with a pulsed source. Yu. M. Buravlev and his co-workers considered in their paper the effect of the structure of an alloy on the result of the analysis of cast irons and steels. New data on the connection between the compositions of the vaporlike and solid phases were given in the communications by O. I. Nikitina, A. M. Shavrin, and co-workers, by E. A. Grinzaida, and A. V. Kozlov with V. P. Pashevkin. In addition, reports were made by G. E. Zolotukhin and his co-workers on the study of thermal processes in the arc electrodes.

A communication by L. I. Topalov on an experiment of a quantitative determination of the effect of "third" components was heard with great interest. The author has developed procedures for determining, with the necessary accuracy, high contents of elements, an important factor in the further extension of practical applications of the methods of spectral analysis.

The problems connected with standards were treated in the papers by S. B. Shubina and A. B. Shaevich, I. V. Matyugina, N. K. Rudnevskii, E. S. Obukhova, and E. V. Levakov, V. G. Prokhorov, V. A. Bobrov, N. A. Sin'lov, and I. S. Fishman.

Experience in the use of photoelectric apparatus for the analysis of alloys and steels was discussed in communications by V. I. Kiselev, K. A. Sukhenko, and co-workers, by V. F. Korotkov and N V. Buyanov and co-workers. A. K. Tumanov has developed and employed photoelectric apparatus for the analysis of iron-foundry slags.

Many communications were devoted to the determination of small impurities in metals and alloys: R. I. Gutkina—on spectrochemical analysis of silicon and nickel of high purity; S. B. Shubina and A. B. Shaevich—on the determination of small harmful impurities of nonferrous metals in iron alloys; A. A. Kuranov—on the analysis of platinum for 18 elements; A. I. Buzaeva and M. G. Velichko—on the analysis of pure compounds of nickel, lead, and bismuth; S. G. Bogomolov, A. I. Mezentsev, and G. P. Kostromin—on the determination of microelements in normal and cancerous tissues, etc.

In papers by M. N. Shtutman devoted to spectral analysis of slags, the effect of the iron composition of silicate alloys on the results of the spectral analysis were considered for the first time. Methods of eliminating this effect were also discussed. The application of the electrochemical theory of structure of molten slags to this problem was found to be quite fruitful. Problems of analysis of nonmetallic substances were considered also in communications by E. N. Lesnikova and A. M. Shavrin with their co-workers.

Several features of the structural analysis of gas mixtures were considered in the paper by N. A. Prilezhaeva.

A communication from V. L. Ginzburg and V. G. Koritskii on a projected GOST standard covering methods of spectral analysis was heard with great interest.

Much of the work of the section on atomic spectroscopy was devoted to an interchange of experience gained by the commercial laboratories in Sverdlovsk, Magnitogorsk, Perm, Stalinsk (Kuzbass), the lower Tagil, and other cities of the Urals and Siberia. In particular, a branch conference was held for the workers in ferrous metallurgy, organized by the Ural Institute of Ferrous Metals.

The use of molecular spectroscopy in the Urals has not advanced sufficiently yet, and therefore the agenda of the section on molecular analysis was somewhat random in character. Papers of an applied nature were in the majority.

S. G. Bogomolov, A. P. Kolesov, N. P. Grebenshchikova, and E. I. Gorbunova reported on a spectral method of analysis of a complex four-component mixture, consisting of o-, m-, and n-xylols and of ethyl benzene. This analysis method is in use in many Ural plants.

A. I. Finkel'shtein gave several reports on his own behalf and on the behalf of a group of colleagues (E. N. Boitsov, B. I. Sukhorukov, T. M. Kornienko, and Yu. I. Mushkin), illustrating once more the significance of methods of molecular spectroscopy to the chemical industry. The following problems were considered: spectro-absorptiometric analysis in the manufacture of diazocyanates, spectral determination of the composition and structure of the products of pyrolysis of melamine, and the use of acid-base properties in the spectral analysis of amino-oxy-compounds. Particular attention was paid to a direct application of the methods developed at chemical plants.

In the solution of many scientific and practical problems, success may be gained with the spectral-chromatographic analysis method, wherein chromatography methods are used to separate various mixtures of substances, while spectral methods are used to identify compounds. Communications by I. M. Birintseva and S. G. Bogomolov reported on the use of this method for the analysis of multicomponent systems of monatomic and diatomic

phenols and its application for the determination of the contents of phenols in run-off water of peat gas-generator stations. I. A Alekseeva, S. S. Spasskii, and T. V. Molchanov devoted their paper to the timely problem of the application of methods of infrared spectroscopy for quantitative estimates of polymerization reactions. V. V. Zharkov and V. N. Kolobova told of a quantitative determination of the residual monomer in polystyrol as determined from ultraviolet spectra.

Another group of communications (I. Ya. Postovskii, V. Ya. Kazakov, N. P. Bednyagin, and L. F. Trefilova) was devoted to the use of infrared spectroscopy in the determination of the chemical structure of several heterocyclic compounds, particularly drugs. I. Ya. Postovskii showed clearly the advantages of the use of methods of molecular spectroscopy in the determination of the fine structure of chemical compounds. In particular, such investigations make it possible to establish even now the connection between the biological action of the compound and its structure.

V. S. Korobkov, using a large group of compounds as an example, reported interesting data on the spectroscopic manifestation of the intramolecular hydrogen bond.

A lecture by A. A. Kolovskii and A. V. Korshunov was devoted to Raman spectra of several heptahydrate alums. The capabilities and the application of Raman spectra for the analysis of mixtures of phenol and chrysols was reported by I. A. Alekseeva and G. A. Semerneva.

A specific feature of the conference was the relative number of papers devoted to the applications of spectroscopy in biology and medicine. S. G. Bogomolov reported on "The Spectroscopy of Blood," in which he cited a large amount of experimental data to demonstrate the advantage of simultaneous measurement of scattering and many other parameters along with measuring the absorption of blood. Such measurements make it possible to trace the dynamics of the system and, in particular, the processes of aggregation and de-aggregation of albumens.

A communication by S. G Bogomolov and F. D. Pemova was devoted to the determination of cancerogenous substances. The variation in the spectra of blood serum under the action of ionizing radiation and low temperature was reported by Yu. K. Ledentsov.

Interesting results were obtained by A. M. Genkin and S. G. Bogomolov on the use of optical methods to determine the mechanism of interaction between albumens and glycogenous liver.

The papers by the Leningrad scientific workers were heard with great interest: K. P. Vasilevskii and B. S. Neporent—"Absorption of Infrared Radiation by Water Vapor in Mixtures with Extraneous Gases;" A. K. Trofimov—"Spectral Luminescent Method of Investigation and Control of Crystal-Chemical Transformations in Solid Phases;" and L. D. Kislovskii—"New Method of Absorption Analysis of Reflection."

The agenda of the section demonstrated that molecular spectroscopy methods have begun to be successfully developed in the Urals. The Conference drafted recommendations aimed at the development of research and applications in the field of spectral analysis in the Urals. The proceedings of the Conference will be published.

S. G. Bogomolov and A. B. Shaevich

FOURTEENTH ROZHDESTVENSKII LECTURE

In accord with the established tradition, the regular lecture in honor of D. S Rozhdestvenskii was held on May 19, 1960 at the State Optical Institute.

Professor M. M. Gurevich delivered a paper on "Work of the State Optical Institute in the Field of Photometry." The lecturer surveyed the fundamental results obtained in the State Optical Institute in the field of scientific and applied photometry. Highlighted among these results were the theory of the photic field (with demonstration of the determination of the light vector), the theory of transmission of light through a scattering medium, different applications of the nephelometric method, methods of measuring small brightnesses, development and adoption of the technology of manufacture of selenium barrier-layer rectifiers, and many photometric and spectrophotometric instruments developed at the State Optical Institute and now manufactured by the optical-mechanical industry.

In a lecture entitled "Light Quanta and Vision," N. I. Pinegin described the quantum nature of peripheral and central vision in dark adaptation, and of central vision in dark adaptation, and of central vision in light adaptation. Extending the method developed by Academician S. I. Vavilov for the observation of quantum fluctuations, the lecturer showed that the threshold number of quanta is independent of the wavelength but does depend on the angular dimensions of the light source. The minimum threshold for rods and cones is two quanta. In dark adaptation, the coefficient of absorption is approximately 1.5 to 3% at the maximum of spectral sensitivity of the rods, and is approximately 0.25 to 0.5% in the maximum cone sensitivity. When the background brightness changes from 4×10^{-4} nt to 5×10^{3} nt, i.e., by a factor 1.3×10^{7}, the area of a dark square against a bright background at unity contrast changes by a factor of 5000, the area of the effective aperture of the pupil changes by a factor of 8, the vision delay time changes by a factor of 4, the coefficient of absorption changes by a factor of 80, and the over-all change is equal to the change in the brightness of the background. The threshold, however, is independent of the brightness of the background and is equal to two, or at any rate a small number of quanta. This confirms the belief of Academician A. A. Lebedev that the resolving power of the eye is limited by quantum fluctuations.

*BOOK REVIEWS**

*Translation editor's note: There are several proper nouns in these reviews which it has not been possible to identify

OPTICS OF THIN-LAYER COATINGS

By G. V. Rozenberg, Fizmatgiz, Moscow, 1958

The last decade has seen widespread use of thin-layered coatings of dielectrics, semiconductors, and metals in optical instrument construction. Their use has not only radically improved the quality of many instruments and systems, but has uncovered the possibility of development of new designs, without which further progress in different branches of physics and engineering is unthinkable. There is no doubt, for example, the the presently produced infrared interference optical filters are bound to revolutionize the field of qualitative and quantitative analysis of molecular compounds, the results being no less valuable than those obtained by the introduction of emission spectral analysis fo manufacturing and scientific practice.

Interference filters, interferometers and Fabry-Perot etalons, light-splitting and transmission-increasing systems, "cold" mirrors and high-efficiency reflectors, or stratified polarizers are but part of a long list of devices in which thin coatings are necessary. The monograph by G. V. Rozenberg "Optics of Thin-Layer Coatings" is devoted to the theory and practical application of such systems. Its publication fills a need for books of this kind, since the anthology "Coating Optics," published as long ago as 1946, dealt only with problems of reducing the reflecting ability of optical parts, and has furthermore become obsolete to a considerable degree.

The monograph consists of two parts. In the first the author considers the optical properties of thin layers, their structural features, methods of calculating single- and multiple-layer coatings, and different theories of two-dimensional colloidal media. The second part is devoted to the theory and practice of multiple-ray interferometry (including interference microscopy), layered interferometers, and interference filters.

The principle feature in his exposition of the theory of coatings is the author's general approach to the rather extensive problem of layered systems. In spite of the numerous descriptions of various procedures and methods of calculation extant in the literature, by which the basic parameters of specific systems or devices can be determined, the problem was never before formulated in so general a form. In this respect the author's approach is original. The advantage of this approach lies firstly in the fact that it permits a serious analysis, with sufficient mathematical rigor, of not only the principal aspects of the theory, but of many sufficiently fine phenomena, which occur upon reflection or transmission of an electromagnetic wave by a layered system. In many cases the formulation of the theory comes up against serious difficulties, which the author always attempts to overcome. Naturally, he does not always succeed, since the monograph touches upon a large circle of problems. It is known, for example, from textbooks and from the scientific literature, that the Fresnel formulas for the amplitudes of the reflection coefficients of the s and p components can be written in two ways, with equal or with opposite signs. The first possibility is used in this monograph, although it is still unclear which possibility actually takes place. The author does not prove his statement that, from the theoretical point of view, his choice is the only correct one By this token, the phase shift between the s and p components would have to be set equal to zero at normal incidence. The author does so in the case of a dielectric (Fig. 46), but when it comes to a metal (Fig. 47) this phase shift is set equal to π for some reason. The question of phase relationships is of principal significance in the theory and practice of coatings, and calls for an exceedingly serious approach.

The development of high-quality interference devices depends in many respects on the structural features of the thin layers, on how they are affected by optical and mechanical characteristics of the production conditions, on extraneous factors, and on the time. Chapter 1 and part of Chapter 5, which is allied to Chapter 1 in its content, is devoted to these problems. Surveying critically extensive source material, the author has succeeded not only in casting enough light on the present day status of the thin layer optics, but has indicated many aspects of practical significance. It must be remembered that the thin layer physics has only recently taken the form of a fully defined field of knowledge. In this connection, many concepts, separate theories, and the treatment of experimentally-observed phenomena call for additional refinement and review on the basis of the new data. It is no wonder, therefore, that it is precisely the first and fifth chapters that contain the most inaccuracies and moot premises. These include, first of all, the explanation of the contradiction between x-ray diffraction and electron-diffraction data on the structure of thin layers, the definition of the concept "thickness of a layer" and an experimental measurement of this thickness by various methods, the description of the process of formation of the layer, the simulation of a single-layer granulated coating, the question of the possibility of defining it in terms of "effective indices" of refraction and absorption, an estimate and limitations of the phenomenological theory and of the microtheory, etc.

A persistent theme in the entire book is the author's statement that it is impossible to simulate a two-dimensional colloid by means of a solid single-layer coating. It is also proposed that the analog of such a colloid can be a system consisting of two layers. The basis for this statement is the Herprin theory, which is obviously unsuited in this case. This theorem is based on the applicability of the phenomenological theory and describes systems that consist of solid layers. Therefore, any model representation of a colloidal layer in no case can be related with the aforementioned theorem, and the problem arising must be resolved in a different manner.

One of the most fundamental problems in the optics of a thin layer (two-dimensional colloid) is whether it can be characterized by means of an "effective" index of refraction or absorption. The author of this monograph denies such a possibility, but in formulating a theory of a two-dimensional colloid he ascribes these parameters

to individual granules (furthermore, of very small size). Nonetheless, the author's theory developed in Chapter 5 adds much to our concept of the two-dimensional colloid. It is there that the theories of Maxwell-Garnett, David-Schopper, and D. V. Sivukhin are discussed and their individual shortcomings and applicability limits are indicated.

The evaluation of the Maxwell-Garnett theory is not quite correct in attributing to it all the vices of the phenomenological theory. In fact, the starting point of the phenomenological theory is the assumption that the layer is homogeneous, whereas the Maxwell-Garnett theory assumes it to be granulated. The most debatable point in the Maxwell-Garnett theory is the assumption that the Lorentz-Lorenz formula is applicable to a two-dimensional colloid.

The energy and phase relations for a variety of single- and multiple-layer coatings are derived in Chapters 3 and 4, which are of considerable interest to persons engaged in the design and preparation of interference devices.

From among the chapters of the second part of the monograph, the richest in contents is the sixth. It contains a detailed development of the theory of the layered interferometer, along with a discussion of its basic optical characteristics (resolving power, contrast, half-width of the fringes, etc.) and a detailed analysis of the factors that influence the quality of the interference pattern. The interference behavior is analyzed for both transmitted and reflected light. Brief information is also given on complex interferometers and multiplexes. The material in Chapter 6 is of particular interest to practicing spectroscopists.

The next chapter is devoted to multiple-ray interference microscopy. It discusses problems in the practical utilization of the interference microscope, such as the study of the surface relief, growth spirals in crystallization, determination of the thickness of coatings (including monomolecular ones), detection of surface fluctuations, etc. In view of the high precision and widespread use of methods of multiple-ray interference microscopy, the next edition of the book should consider these problems in greater detail.

The theory of phase contrast, which has become one of the most effective methods of investigation of biological objects, is treated too abstractly. Through the use of several model representations, the first section of Chapter 7 could be made to be understood by a wide circle of biologists and physicians.

The last, eighth, chapter is principally devoted to the practical utilization of interference filters operating both in transmission and in reflection. The theory of such a filter is analogous to the theory of the layered interferometer (Chapter 6), and consequently the author does not treat it separately.

Interference-polarization filters, an examination of which concludes the monograph, do not contain thin-layered coatings at structural elements, but their operating principle fully justifies their inclusion in the monograph.

Summarizing, the book "Optics of Thin-Layered Coatings" is a valuable manual not only for specialists directly engaged in the calculation, design, and construction of layered systems, but also for researchers working in various branches of physical optics, applied optics, and spectroscopy.

M. P. Lisitsa

POLARIZED LUMINESCENCE OF ATOMS, MOLECULES AND CRYSTALS

By P. P. Feofilov, Fizmatgiz, Moscow, 1959

Polarization of luminescence is one of the basic properties of radiation. It permits a determination of the nature and properties of the radiator and of its location in the medium. It makes it possible to follow the motion of an entire excited molecule or its parts, and to follow the migration of the excitation energy. These broad possibilities for the study of matter, offered by the investigation of polarization of luminescence, are extensively used at present to solve many scientific and practical problems.

In view of the importance of polarization phenomena, they have been the subject of many papers published in various journals, but not one monograph has appeared to summarize these researches. Nor did the author of the monograph reviewed here, P. P. Feofilov, undertake at first this large task. He writes in the foreword: "The exposition is based on the author's own researches, already extensively reported in original and survey articles. The material gleaned from the literature is introduced as a rule only where necessary to unify the exposition and to consider all problems from a single point of view".

Feofilov's researches in the field of polarized luminescence have touched upon many aspects of the phenomenon and have made a considerable contribution to the study of polarization of luminescence of solutions of complex molecules, and particularly the luminescence of cubic crystals. The author's intention must therefore be conceded to be correct; even in the limited form indicated, the monograph would be of undoubted interest and worthy of publication. Actually, however, in writing this book the author has so expanded the circle of topics considered, that its content begins to correspond to a greater degree to the broad title of the book, "Polarized Luminescence of Atoms, Molecules, and Crystals." This has rendered the book interesting not only to specialists engaged in polarized luminescence, but to a wider circle of readers attempting to gain an idea of the general state of this field of science.

The monograph comprises seven chapters. The first, "Elementary Radiators and Polarization of Radiation," with fifty four pages, reviews the polarized-luminescence phenomena connected with the properties of elementary radiators. This chapter is a concise but very valuable survey of different occurrences of polarization of luminescence along with their classical and quantum-mechanical interpretation. The second chapter, "Polarization of Resonant Radiation and of Atomic Fluorescence," is devoted to the polarization of radiation of atoms in gases. Considered here are the classical and quantum-mechanical theory of polarization of resonant radiation, the polarization of atomic fluorescence, the effect of collisions on polarization of resonant radiation, and the fluorescence of atoms. More than half of the chapter is based on the author's original papers, some published here for the first time. In particular, the degree of polarization of resonant radiation is given as a function of

the quantum number J, the concept of circular radiation is introduced and its value is calculated, and other topics are treated. The chapter contains fifty two pages.

This is followed by a short chapter (seventeen pages) on "Polarization of Luminescence of Diatomic Molecules," in which the classical and quantum theory of the radiation polarization of such molecules is given, together with experimental material pertaining to the study of this phenomenon. The effect of collisions on polarized luminescence of diatomic molecules is also considered. Worthy of note is a quantum-theoretical analysis of radiation polarization of diatomic molecules, published here for the first time, which makes quantitative calculations of polarization possible.

Chapters 4, 5, and 6 contain much original material. In Chapter 4 (pp. 121-187), "Polarized Luminescence of Complex Molecules," particular attention is paid to the connection between polarization and the anisotropy of the structure of absorption and radiation centers.

The central problem is that of polarization spectra, in the investigation of which the author's research occupies a prominent place. The effect of the mutual placement of absorption and radiation oscillators and their dependence on the structure of the molecule are considered here. The last sections of the chapter are devoted to a question thoroughly investigated by Soviet scientists—the effect of rotational motions of the molecules themselves in solutions and of the concentration of molecules on the polarization of their radiation, and also to a development of polarized luminescence in systems of metastable molecules.

In Chapter 5 (pp. 187-232) polarized radiation of crystals is considered. After studying the azimuthal variation of luminescence polarization of different cuts of crystals, Feofilov makes extensive use of his results to determine the placement of electron radiators in cubic crystals. Feofilov succeeded in his work in establishing that these crystals are anisotropic in the arrangement of the radiators, which are located along symmetry axes of different orders. The research performed solves the problem completely in many cases and yields highly convincing results.

The last section of Chapter 5 is devoted to a thorough analysis of anisotropic photochemical processes in cubic crystals. Anisotropy of chemical action is due to an anisotropic arrangement of the absorbing systems, which leads to an essentially photochemical change in the correspondingly placed absorbing oscillators.

Chapter 6 (pp. 233-266) is devoted to the connection between multipolarity of elementary radiators and observed polarization of radiation. It describes the work of S. I. Vavilov, of the author himself, and of other Soviet authors, wherein conclusions regarding the multipolarity of the radiators can be drawn from the form of the polarization patterns. This method can be used to establish the nature of the radiator in cubic crystals.

The seventh and last chapter "Experimental Methods and Investigations of Polarization of Radiation" is short and contains a description of instruments and devices used by different workers to investigate the degree of polarization.

The monograph concludes with a bibliography containing 257 titles.

This book is well balanced in treating both the experimental and the theoretical aspects of the problem. It can be readily understood by a wide circle of readers with a certain knowledge of optics, such as university graduates who specialized in optics or senior optics students. But even specialists and scientists working in the field of polarization of radiation will find in it much that is new and useful. The monograph is clearly written and in good style.

A few shortcomings can be pointed out. While Chapters 1, 3, and 4 are concise, Chapter 6 and, more so, Chapter 5 could be condensed. Furthermore, from the point of view of the general theory of polarization luminescence, there is obviously not enough light thrown on questions of polarized luminescence of anisotropic crystals. Only one paragraph is devoted to the very interesting research of Hellwege, which has made it possible to establish the nature of elementary radiators of rare-earth ions in many anisotropic crystals. No mention is made at all of the important work by D. Seedman, N. D. Zhevandrov, and a few others.

It is also regrettable that little space has been given to the effect of motion of the oscillators both in solvents and in crystals. Almost nothing is said regarding exciton energy transfer and its connection with polarization of glow.

Certain omissions should be indicated. For example, Subsection "G" of Section 4 of Chapter 1 (pp. 52-53) contains no reference to the work by S. I. Vavilov, B. Ye. Svechnikov, and A. N. Sevchenko. The equation for the radiation of a vibrating oscillator (p. 134)

$$P_0 = (9\varepsilon - 12\varepsilon + 4) : (3\varepsilon^2 - 4\varepsilon + 8),$$

where $\varepsilon = \overline{\sin^2\gamma}$, and γ is the angle of rotation of the oscillator axis, is attributed to Jean Perrin and A. Yablonskii. Perrin did not work on this problem at all, and Yablonskii derived this formula in 1949, i.e., twenty four years after the author of this book review.

These and a few other accidental omissions are, however, obviously of secondary significance. As a whole there is no doubt that the publication of this very good monograph by P. P. Feofilov, which will prove very useful to all those engaged in luminescence, is to be welcomed.

V. L. Levshin

LETTERS TO THE EDITOR

A DIRECT EXPERIMENTAL CONFIRMATION OF THE SECOND POSTULATE OF THE SPECIAL THEORY OF RELATIVITY

(in connection with Dingle's note)

A. M. Bonch-Bruevich

Received 18 February 1960

It is well known that the Special Theory of Relativity is based on the postulate of the relativity of motion and the postulate that the velocity of light is constant.[1] The first postulate is a direct consequence of the negative results of repeated attempts to detect a privileged coordinate system in observing optical and electrical phenomena. Experiments for this purpose, repeated over several decades after the formulation of the Special Theory of Relativity, have confirmed the first postulate with increasing accuracy.[2-5] The second postulate of the Theory was not based on direct experimental results, and in the decades that followed it was not confirmed directly because of the great difficulties encountered in setting up the appropriate experiments.

The Special Theory of Relativity no longer needs any additional support. None the less, as Academician S. I. Vavilov pointed out more than ten years ago, a direct experiment showing that the velocity of light is independent of the velocity of the source of radiation relative to the observer is important, due to the basic significance of this postulate. Dingle published a note on this recently.[6] It appears from this note that the author is not acquainted with the results of the experiment to confirm the second postulate directly, carried out in 1955.[7-9]

In this experiment, a comparison was made of the times t_1 and t_2 required for light emitted by two moving sources to traverse a distance L = 2000 meters. The sun's equatorial edges were used as sources. Switching from the radiation of the sun's eastern edge to that of its western edge corresponds to changing the velocity of the source of radiation by 3.9 km/sec in the plane of the ecliptic. We used a phase method to show to the required accuracy that under these conditions the transit time over the base L remains constant. The intensity of the light radiated along the base by the left or right equatorial edges of the sun was modulated at a frequency of about 12 Mc/s. The phasemeter of a high resolving-power fluorometer was then used to measure the phase shift $\Delta\varphi$ of the modulation of the light traveling along the base when the transition was made from one edge of the sun to the other.[10]

A statistical analysis of the results of more than 1700 measurements of $\Delta t = t_2 - t_1$ showed that in our experiment the change in the transit time over the base L of the light emitted by the left and right equatorial edges of the sun was $\Delta t = (1.4 \pm 5.1) \times 10^{-12}$ sec.

We note that if the classical law of compounding velocities were valid, the quantity Δt for our apparatus would have had the value 75×10^{-12} sec, which lies far outside the limits of experimental error. In addition, the value $\Delta t = 0$ lies inside these limits.

As was shown,[9] these experimental results can be statistically analyzed along different lines, and used to compare the probabilities that the classical or relativistic laws of compounding velocities are valid. This shows that the probability that the velocity of light is independent of the velocity of motion of the source exceeds by 10^{45} times the probability that the classical law of compounding velocities is valid.

The experimental results appear convincing to us, and it seems of little importance to repeat them in another variation at present (for instance, using excited atoms or ions as a moving source of radiation).

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COMPETITION FOR THE S. I. VAVILOV GOLD MEDAL

The Physico-Mathematical Sciences Division of the USSR Academy of Sciences announces a competition for the S. I. Vavilov Gold Medal, the next award of which will be made on March 24, 1961. This medal is awarded once every three years for outstanding work in the field of physics, and only individual Soviet scientists are eligible to compete for it.

Candidates for the Gold Medal award may be nominated by scientific establishments of the USSR and United Republics (scientific research institutes and laboratories), by design offices, by higher educational establishments, by scientific and engineering societies, and by honorary, active and corresponding members of the USSR Academy of Sciences.

Organizations and individuals nominating candidates for the Gold Medal should submit the following documents to the S. I. Vavilov Gold Medal Jury:

1. Published scientific papers, documents on a scientific discovery or on an invention, in triplicate.
2. Documentary evidence of the opinion of the scientific community on the work submitted.
3. A dissertation by the candidate on the work, not more than a quarter of an author's sheet in length.
4. Short curricula vitae on the candidate enumerating his main scientific work.

Work that has received an earlier prize will not be accepted for the competition.

The papers, with the inscription "For the S. I. Vavilov Gold Medal," should be sent to the S. I. Vavilov Gold Medal Jury at The Physical Institute of the USSR Academy of Sciences, V-17 GSP, 53 Lenin Prospect, Moscow.

Papers must be submitted before December 24, 1960.

OSA CHARTER FLIGHT 1961

EUROPE JULY 1961

You will have read in JOSA that OSA hopes to arrange a charter flight to Europe for the month of July 1961, for members attending the Paris and London ICO Meetings. These are:

PARIS: 5 through 8 July 1961 on OPTICAL MATERIALS, organized by the French National Committee for Optics and Professor André Maréchal

LONDON: 11 through 14 July 1961 on OPTICAL INSTRUMENTS AND TECHNIQUES, organized by a sub-committee of the British National Committee for Optics under the chairmanship of Mr. K. J. Habell

We contemplate a flight leaving New York (Idlewild) on Saturday 1st July for PARIS, and returning from LONDON Airport on Sunday July 30th to New York. Members would make their own way between Paris and London. Informal tours of laboratories in Paris and London may be arranged. It is necessary to make arrangements for such flight within the next month or two, so we need now an expression of interest (without commitment, of course) from members. Members who are interested in principle should return the bottom half of this page to the Executive Office as soon as possible, or hand it in at the Registration Desk during the course of the Boston Fall Meeting. The round trip fare—New York - Paris - London - New York—would be about $275.

MEMBERS WHO HAVE ALREADY INDICATED THEIR INTEREST
NEED NOT WRITE AGAIN

LOS ANGELES OSA MEETING OCTOBER 1961

We could also arrange charter flights from say, Boston, New York and Washington to Los Angeles for the 1961 Fall Meeting, but as it is not yet possible to charter a jet, members may prefer to gain the time. A non-jet flight would take about 10 hours; dates would probably be to leave for LA on 11th and return on 15th October. Fare would be around $150.

REPLY

CHARTER FLIGHTS JULY AND OCTOBER 1961

I am interested in principle in a charter flight N.Y.-Paris-London-N.Y. July 1961 ☐
I am interested in principle in a charter flight to Los Angeles from Boston/New York/ Washington (delete which city is not applicable) October 1961 ☐

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EDITOR'S NOTE

Comments on the scientific content of the translated Russian articles published in OPTICS AND SPECTROSCOPY are invited. They should be addressed as a Letter to the Editor of the Journal of the Optical Society of America and forwarded to the Editor of that journal, Dr. W. R. Brode, National Bureau of Standards, Washington 25, D.C.

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